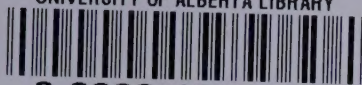


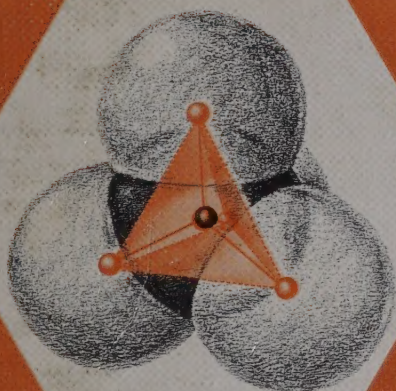
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KEYS TO CHEMISTRY

ELAINE W. LEDBETTER • JAY A. YOUNG



CURRICULUM

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TABLE OF ATOMIC WEIGHTS

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	(227)	Mercury	Hg	80	200.6
Aluminum	Al	13	27.0	Molybdenum	Mo	42	95.9
Americium	Am	95	(243)	Neodymium	Nd	60	144.2
Antimony	Sb	51	121.8	Neon	Ne	10	20.2
Argon	Ar	18	40.0	Neptunium	Np	93	(237)
Arsenic	As	33	74.9	Nickel	Ni	28	58.7
Astatine	At	85	(210)	Niobium	Nb	41	92.9
Barium	Ba	56	137.3	Nitrogen	N	7	14.0
Berkelium	Bk	97	(249)	Nobelium	No	102	(254)
Beryllium	Be	4	9.0	Osmium	Os	76	190.2
Bismuth	Bi	83	209.0	Oxygen	O	8	16.0
Boron	B	5	10.8	Palladium	Pd	46	106.4
Bromine	Br	35	79.9	Phosphorus	P	15	31.0
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.1
Calcium	Ca	20	40.1	Plutonium	Pu	94	(242)
Californium	Cf	98	(251)	Polonium	Po	84	(210)
Carbon	C	6	12.0	Potassium	K	19	39.1
Cerium	Ce	58	140.1	Praseodymium	Pr	59	140.9
Cesium	Cs	55	132.9	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.5	Protactinium	Pa	91	(231)
Chromium	Cr	24	52.0	Radium	Ra	88	(226)
Cobalt	Co	27	58.9	Radon	Rn	86	(222)
Copper	Cu	29	63.5	Rhenium	Re	75	186.2
Curium	Cm	96	(247)	Rhodium	Rh	45	102.9
Dysprosium	Dy	66	162.5	Rubidium	Rb	37	85.5
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.3	Samarium	Sm	62	150.4
Europium	Eu	63	152.0	Scandium	Sc	21	45.0
Fermium	Fm	100	(252)	Selenium	Se	34	79.0
Fluorine	F	9	19.0	Silicon	Si	14	28.1
Francium	Fr	87	(223)	Silver	Ag	47	107.9
Gadolinium	Gd	64	157.3	Sodium	Na	11	23.0
Gallium	Ga	31	69.7	Strontium	Sr	38	87.6
Germanium	Ge	32	72.6	Sulfur	S	16	32.1
Gold	Au	79	197.0	Tantalum	Ta	73	180.9
Hafnium	Hf	72	178.5	Technetium	Tc	43	(99)
Helium	He	2	4.0	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.0	Thallium	Tl	81	204.4
Indium	In	49	114.8	Thorium	Th	90	232.0
Iodine	I	53	126.9	Thulium	Tm	69	168.9
Iridium	Ir	77	192.2	Tin	Sn	50	118.7
Iron	Fe	26	55.8	Titanium	Ti	22	47.9
Krypton	Kr	36	83.8	Uranium	U	92	238.0
Lanthanum	La	57	138.9	Vanadium	V	23	50.9
Lawrencium	Lr	103	(256)	Wolfram	W	74	183.9
Lead	Pb	82	207.2	(Tungsten)			
Lithium	Li	3	6.9	Xenon	Xe	54	131.3
Lutetium	Lu	71	175.0	Ytterbium	Yb	70	173.0
Magnesium	Mg	12	24.3	Yttrium	Y	39	88.9
Manganese	Mn	25	54.9	Zinc	Zn	30	65.4
Mendelevium	Md	101	(256)	Zirconium	Zr	40	91.2

Note: The atomic weight for each element is based on the carbon-12 scale. Parentheses denote atomic weight for most stable or best known isotope.

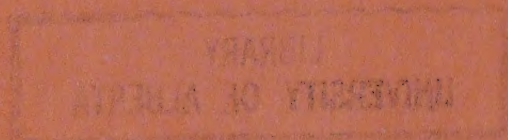
KEYS TO CHEMISTRY

ELAINE W. LEDBETTER • JAY A. YOUNG



ADDISON-WESLEY PUBLISHING COMPANY

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COMPONENTS OF THE KEYS TO CHEMISTRY PROGRAM

Text

Laboratory Manual

Teachers' Guide

Tests

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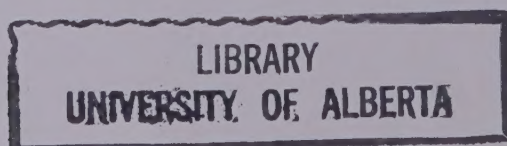
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TO THE STUDENT

KEYS TO CHEMISTRY is a course designed especially for you. We have learned that there are many students like yourself who want to know what chemistry involves and how it relates to their daily lives. They also want to study chemistry without becoming lost in theory and the memorization of facts. This program is planned to accomplish these goals. Mathematical calculations are used only when needed to perform experiments or to interpret laboratory results. You will be introduced to most of the concepts right in the laboratory, as you do the experiments in the accompanying laboratory manual. You will observe reactions and propose hypotheses about the results before you read the discussion in the textbook.

The textbook is written in a way that lets you use your own style of learning; you can move through the course in an independent way, at a pace comfortable for you. Each chapter begins with a list of objectives for the chapter and a suggested order of study. You can use the objectives and the order of study like a road map to plan your journey into chemistry. The activities are designed to enable you to master the stated objectives. Practice Exercises and a Self-Test are included at the end of each chapter. Use them to help you know when you are ready to be tested on any part of the material. Answers to the Practice Exercises and the Self-Tests are included at the end of the book.

You are encouraged to design experiments, to write essays and poems related to chemistry, to produce bulletin boards and posters, and to do other kinds of original work. Suggestions for such creative activities are given at the end of each chapter. These are simply suggestions; use them as they are or as a springboard for your own ideas.

Many people have contributed to the development of this course. We are grateful to the Pampa, Texas, Superintendent of Schools, Dr. James F. Malone, and to the Pampa Senior High School Principal, H. Cameron Marsh, Jr., for their constant support and encouragement. Students Debbie Veale and Johnny Merilatt drew the illustrations for the preliminary edition. Student Chris Dunham is to be especially commended for designing Experiment 2-5. Students Jeannie Fischer and Rebecca Winter provided the answers to the Practice Exercises and the Self-Tests. Many of the innovations in both the textbook and the laboratory manual are the result of suggestions made by Pampa Senior High School students; their enthusiastic assistance made this book possible. We are grateful to Jean Casey, a fellow teacher, for the many long hours she spent typing the manuscripts for the preliminary and final editions.

Many other students and teachers helped us bring the material to its present standard by using it in its preliminary forms. Two of the most helpful teachers in this group are Miss Eleanor Jacomet (Mrs. Howard E. Williams) of Ecourse High School, Ecourse, Michigan, and Mrs. Daisy Nell Huntsinger, Hereford High School, Hereford, Texas. We express our gratitude for the assistance we have received from innumerable sources.

*Elaine W. Ledbetter
Jay A. Young*



Elaine W. Ledbetter at high school graduation . . . in her first year of teaching

. . . today

As you read a textbook, do you stop to think about the authors? Do you realize that there are real persons behind the type and the illustrations on the pages of the book? Someone had to write the book; someone had to feel that they had important contributions to make to the education of others.

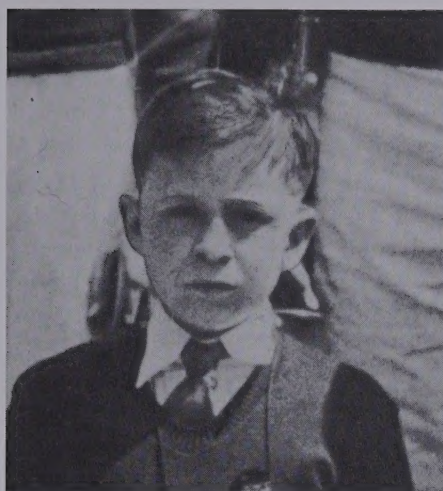
In the case of *KEYS TO CHEMISTRY*, Elaine Ledbetter got the project started. In her school, too few students were taking chemistry; she felt that she had to do something to attract more students into studying this important portion of human knowledge. She, in fact, feels that chemistry needs to be a part of every student's education. After several years of successful testing of preliminary materials which led to increased enrollment in chemistry in her own school, Mrs. Ledbetter decided to prepare the text and laboratory manual that comprise *KEYS TO CHEMISTRY*.

She enlisted the aid of Dr. Jay A. Young, Hudson Professor of Chemistry at Auburn University, Auburn, Alabama. Between them, Mrs. Ledbetter and Dr. Young have over sixty years of experience as teachers of beginning chemistry, one at the high school level and the other at the college level. This experience has given them a sympathetic understanding of beginning chemistry students and how to help them learn chemistry.

KEYS TO CHEMISTRY represents the authors' efforts to use their understanding of the learning process to help you have an enjoyable, stimulating, and profitable learning experience with chemistry.

Elaine W. Ledbetter graduated from high school in 1934, obtained a bachelor's degree from the University of Oklahoma, and began her teaching career in 1940. She earned her master's degree at North Texas State University in 1954. She has received awards in recognition of her teaching excellence: she was named Outstanding Chemistry Teacher in Texas; Texas Teacher of the Year; listed on the Look Magazine National Teacher of the Year Honor Roll; and given the first James Bryant Conant Award, Fifth District of the American Chemical Society. She has also been an important contributing member in a number of professional associations. She has served as president of the Science Teachers Association of Texas, as both secretary and president of the

ABOUT THE AUTHORS



Jay A. Young in high school



...as a graduate student



...today

National Science Teachers Association, and as a member of the International Science Fair Advisory Committee.

Jay A. Young obtained a bachelor of science degree from Indiana University in 1939, a master of arts degree from Oberlin College in 1940 and a doctor of philosophy degree from Notre Dame in 1950. One of his former students said about him: "His energy and impact upon the undergraduate college chemistry curriculum has been nothing less than six on the Richter scale of seismic shock."

Dr. Young is a prolific contributor to both college and high school chemistry teaching as an author of articles, textbooks, and laboratory manuals, as an organizer of conferences for chemistry teachers, and as the chief reader for the Advanced Placement Chemistry Program. He is a member of the American Chemical Society (ACS) and a fellow of the American Association for the Advancement of Science.

Dr. Young has received the Notre Dame Centennial of Science Award and the Award for Excellence in the Teaching of Chemistry given by the Manufacturing Chemists Association. He is a past chairman of an ACS section and has served as secretary of the Division of Chemical Education of ACS. He was a member of the Advisory Council on College Chemistry from 1963 to 1968.

You can see that both Mrs. Ledbetter and Dr. Young have led busy, productive adult lives. The most important and most rewarding part of their lives has been the many days they have spent in classrooms and laboratories in contact with students like you. They have been successful teachers in their direct contact with students. Now they hope to contribute to the success of a great many more students through this book. They would like to know your judgment of whether they have been successful. They would welcome your suggestions for improvements in this book and would like to know what you like best about it. Write to them in care of the Science Publishing Group, Addison-Wesley Publishing Company, Menlo Park, Ca. 94025 next spring after you have finished this excursion into chemistry.

The Editors

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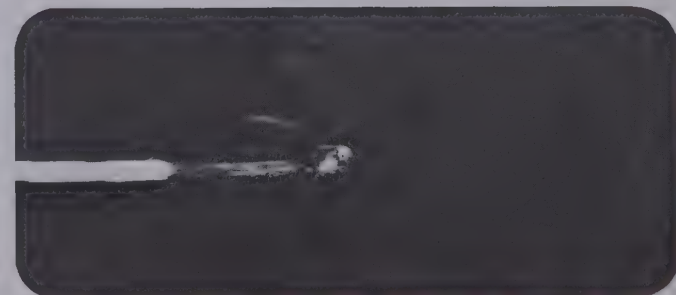
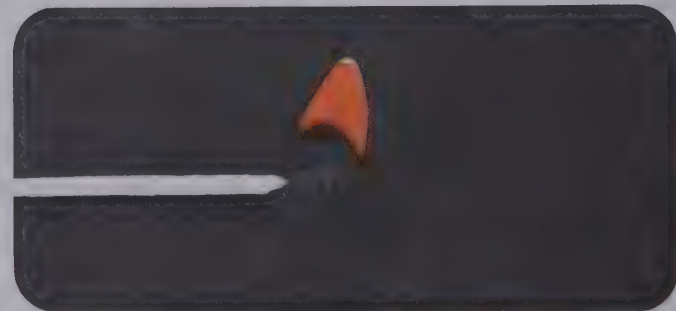
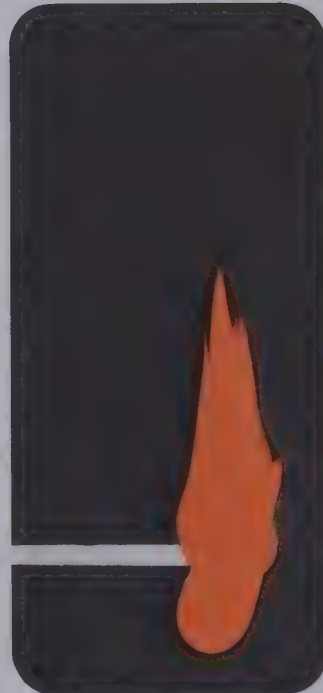
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THE A, B, C's OF CHEMISTRY: ATTITUDES, BUILDING BLOCKS, AND CONCEPTS

OBJECTIVES:

By the time you have completed your work on Chapter 1, you will be expected to demonstrate acceptable performance on the following objectives.

1. *Identify* on sight the apparatus commonly used in the laboratory.
2. *Spell* correctly the names of the apparatus commonly used in the laboratory.
3. *Describe* and *demonstrate* the proper techniques for use of the various laboratory apparatus.
4. *State* ten safety rules which should be observed in the laboratory and *cite* the reason for each rule.
5. *Classify* statements from a given list as: (a) hypothesis, (b) observation, (c) interpretation or inference, (d) conclusion.
6. *Read* any balance in the laboratory to the proper number of significant figures.
7. *Read* any graduate in the laboratory to the proper number of significant figures.
8. *Calculate* the percentage error when given data from an experiment and the accepted value for the property involved.
9. *Determine* the density of a solid, regular or irregular, by any method you choose when provided with the necessary equipment.
10. *Calculate* the mass, volume, or density of an object from the formula for density, given any two of the variables.
11. *Graph* a set of data; *label* all parts of the graph appropriately; *determine* the slope of the line; and *apply* the mathematical equation for the line.
12. *Interpret* a graph of data. This includes ability to *identify* the dependent and independent variables, *determine* the slope of the line, *state* the relationship that exists between the variables, and *apply* the mathematical equation for that type of line.
13. *Solve* problems involving use of significant figures.
14. *Locate* information in the *Handbook of Chemistry and Physics*, given a specific question.
15. *List* current journals and periodicals available for reference in chemistry.
16. *Define* the units in the International System of Units.

SUGGESTED ORDER OF STUDY

1. Study the section in the laboratory manual showing common laboratory apparatus and become familiar with the name and spelling of each piece.
2. Identify the apparatus in your laboratory desk.
3. Study the laboratory techniques pictured and described in the laboratory manual and practice those with which you are not familiar.
4. Study Sec. 1-1 and 1-2 in this textbook on the procedures of scientific problem solving.
5. Perform Exp. 1-1. Prior to going to the laboratory, be sure to prepare your laboratory record book according to suggestions given.
6. Hand in a formal report on Exp. 1-1.
7. Have your plans for further investigations, which you suggest in your formal report for Exp. 1-1, approved by your instructor. After approval, carry out your investigations in the laboratory.

8. Hand in a formal report on your investigations.
9. Read about the work of a scientist and see if you can separate his work into the procedures of observation, interpretation, inference, hypothesis, prediction, and experimentation. Antoine-Laurent Lavoisier, Robert Boyle, John Dalton, J. J. Thomson, and Albert Einstein are suggestions. Some sources of information about their work are: *Encyclopaedia Britannica*, *Journal of Chemical Education*, the magazine *Chemistry*, and the book *Introduction to Concepts and Theories in Physical Science*, by Gerald Holton, published by Addison-Wesley, Reading, Mass., 1952.
10. Study Secs. 1-3 through 1-8 of this textbook. Solve practice problems. Practice making measurements of length, mass, and volume in the laboratory if needed.
11. Study Secs. 1-9 and 1-10 on variables in experimental work and graphing.
12. Perform Exp. 1-2.
13. Hand in a formal report on Exp. 1-2.
14. Study Sec. 1-11 on the concept of density. Handle many different objects in order to become familiar with the concept of density.
15. Perform Exp. 1-3. Note: This experiment requires advance planning on how you will determine the density of different objects.
16. Hand in a formal report on Exp. 1-3.
17. Study Secs. 1-12 and 1-13.
18. Perform Exp. 1-4.
19. Hand in a formal report on Exp. 1-4.
20. Do Exercise 1-1 on learning to use the *Handbook of Chemistry and Physics*.
21. Do the Practice Exercises in preparation for the Self-Test.
22. Take the Self-Test and score your own work. Be sure to review any topics on which you are uncertain.
23. Take the final test on Chapter 1.

1-1 • CHEMISTRY AND DAILY LIVING

Why do leaves change color in the fall? Why does ice float in water? When you strike a match, what is happening in the half-second or so before the match catches fire? Why does a carbonated beverage fizz when salt is sprinkled into it? Can man control the effects of pollution? How does glue make things stick together? Bread and cheese are foods; wood is not; why? What makes a stone different from a piece of iron? How is iron made? Where does it come from? What makes a copper penny different in color from a dime or a quarter? Have you ever wondered about such questions? They can be answered by scientific investigation, and by applying what you learn from those answers.

Chemistry is that branch of science particularly concerned with matter and its changes. What is matter? Iron and stone are both matter. Why are they different? Why does matter change? Iron rusts; stones crumble: a piece of limestone will fizz if vinegar is poured over it. How can we explain such changes? How can we explain other changes we observe? How do leaves change color in the fall?



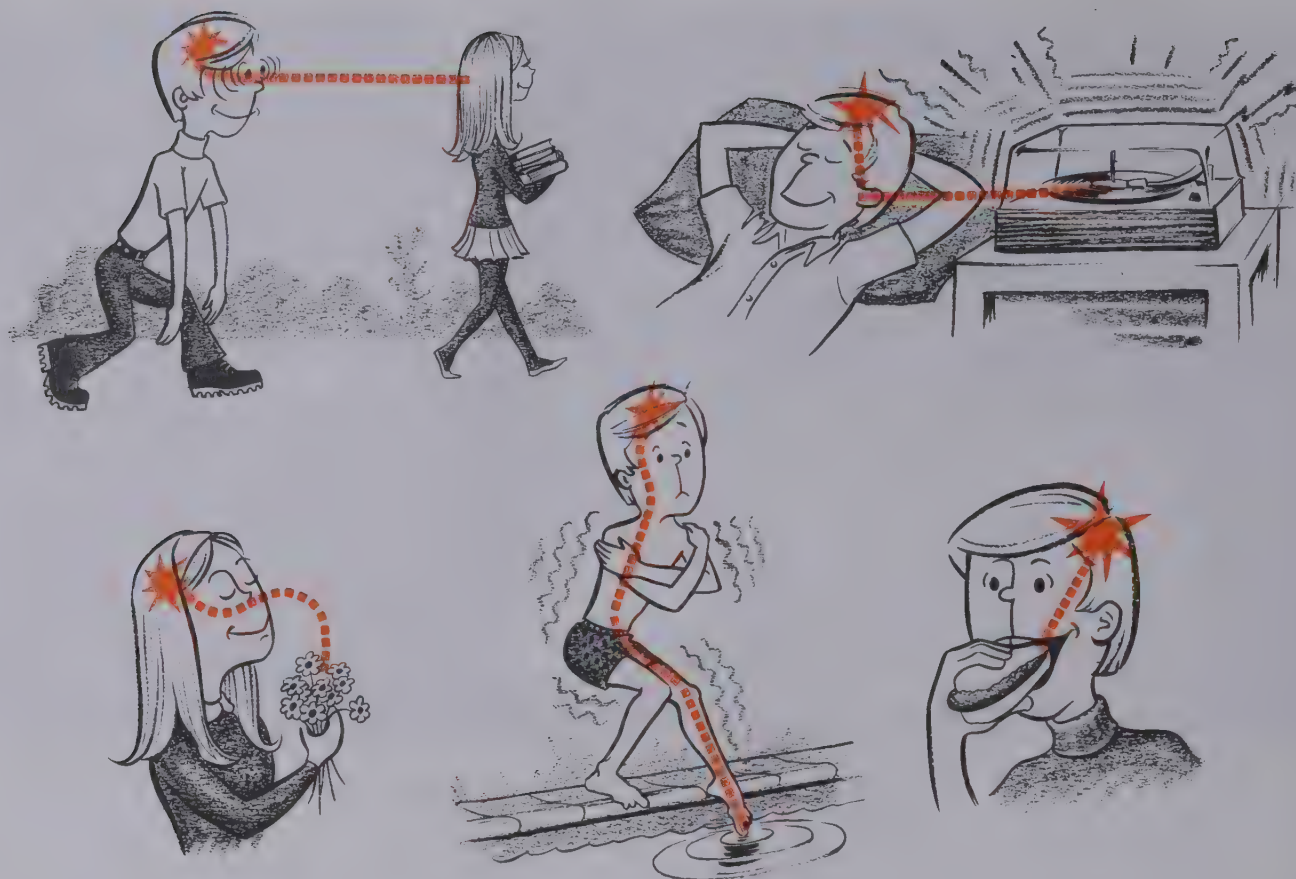
Putting a few drops of acid on a rock is a way to test whether the rock is made of limestone.

Laboratory experimentation, a way of studying changes, provides the foundation upon which you can build an understanding of chemistry. As you make observations and gather data in the laboratory, search for patterns in the observations you make.

Suppose you make a laboratory study of the striking of a match. Try to strike a match by using the wrong end. The pattern, the regularity, we observe is discouraging; the match won't light. Using the head end this time, try to strike a match on a piece of glass, or try to make the match light by pulling the head through a pile of sand. Again the same result. What is there about the head of a match which requires that it be rubbed briskly across a firm, rough surface? Closer, more complete observation might reveal the patterns. From all these observations we might propose an explanation for the action that we observe in our laboratory investigation.

1-2· HOW TO MAKE LABORATORY INVESTIGATION MEANINGFUL

There is no magic formula for solving a problem in the laboratory. There are as many ways to go about it as there are people who engage in scientific investigation. However, certain attitudes and procedures become apparent when we examine the work of scientists. While the order in which the attitudes and procedures are used may vary widely, there are overall patterns that are characteristic of laboratory investigation. It is important that you become aware of these patterns.



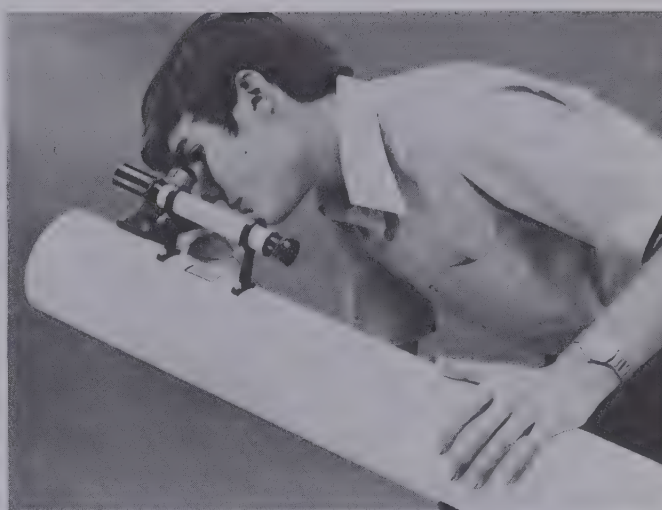
Sensory messages.

Observation

To observe means to notice. Therefore, to become a good observer, you must make the fullest use of your senses. Curiosity and an inquiring mind are essential to making complete observations. Observe a pencil: How many different observations can you make? More than one hundred are possible, if you very patiently and intensely look, listen, and touch.

Of course, becoming a good observer requires practice as well as patience. To make very thorough observations, scientists often use instruments to





Meaningful scientific observations usually require the use of instruments.

aid their senses. A magnifying glass and a magnet can be useful in making observations of a pencil. Certainly you would want to use a ruler or a pair of calipers or both. You might wish to use a thermometer. What could you learn by using each of these instruments as you observe a pencil?

Microscopes enable us to see particles which are far too small for the unaided eye to detect; it would be helpful to use a microscope in making detailed observations of a pencil. Astronomers use another optical instrument, a telescope (not of much use for a pencil), when they observe the stars, or the moons of the planet Jupiter. Cameras are another kind of instrument useful in observing a pencil, although not absolutely necessary; in exploring the moon, astronauts do need and use cameras very extensively.

Other instruments supplement other senses; for example, a physician uses a stethoscope to aid his sense of hearing when he makes observations of the condition of a person's heart or lungs. In their observations, scientists use many kinds of instruments that will expand their ability to observe; quite often, instruments must be invented.

Instruments are also important because they make the difference between *qualitative* observations and those that are *quantitative*. Qualitative information involves no measurement, whereas quantitative information tells how much, how fast, how large, how hot, and so on.

For example, compare these two observations:

- a. A piece of aluminum foil placed in hydrochloric acid produces a gas and heat.
- b. A 1-cm \times 3-cm strip of aluminum foil placed in 10 ml of concentrated hydrochloric acid produces a rapid evolution of gas and causes the temperature of the mixture to rise 20°.

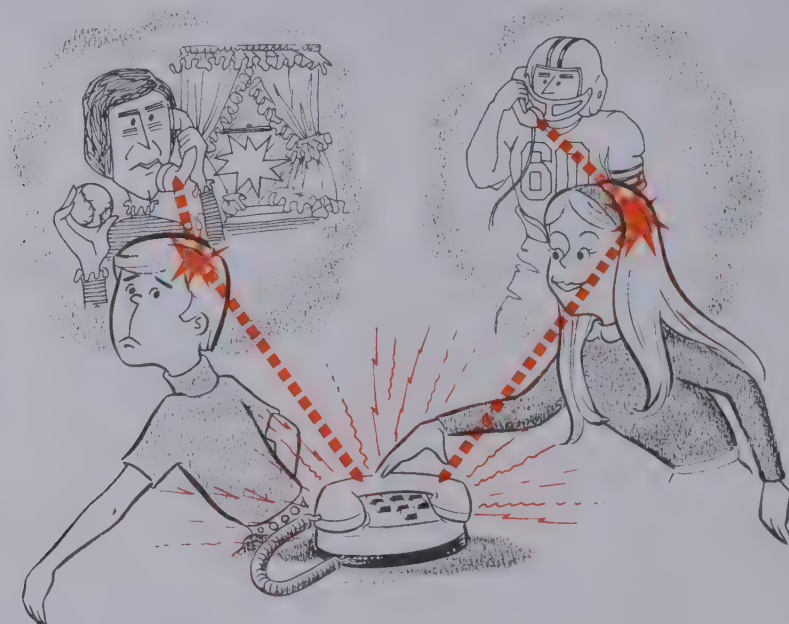
An observation is a statement of fact without any attempt to explain what has been observed. Sometimes it is necessary to make a great number of observations before we can use them in solving a problem. When we have enough observations, we can examine them for patterns and regularities that lead us to another procedure, that of interpretation, or inference.



Interpretation and Inference

Proper use of observations requires reasoning and experience. For example, if your dog begins to bark in the middle of the night, you may *infer* that a prowler is in the immediate vicinity. The fact that your dog barks is an observation. Your attempt to explain *why* he is barking is an inference, or an interpretation of the fact. You could not infer that he is barking at a prowler unless you had previous experience with his pattern of behavior in a variety of circumstances. A young child would not make this inference, because his experience with dogs and prowlers is inadequate.

Both observation and interpretation are important procedures in scientific problem solving, but *they are different and we must not confuse them.*



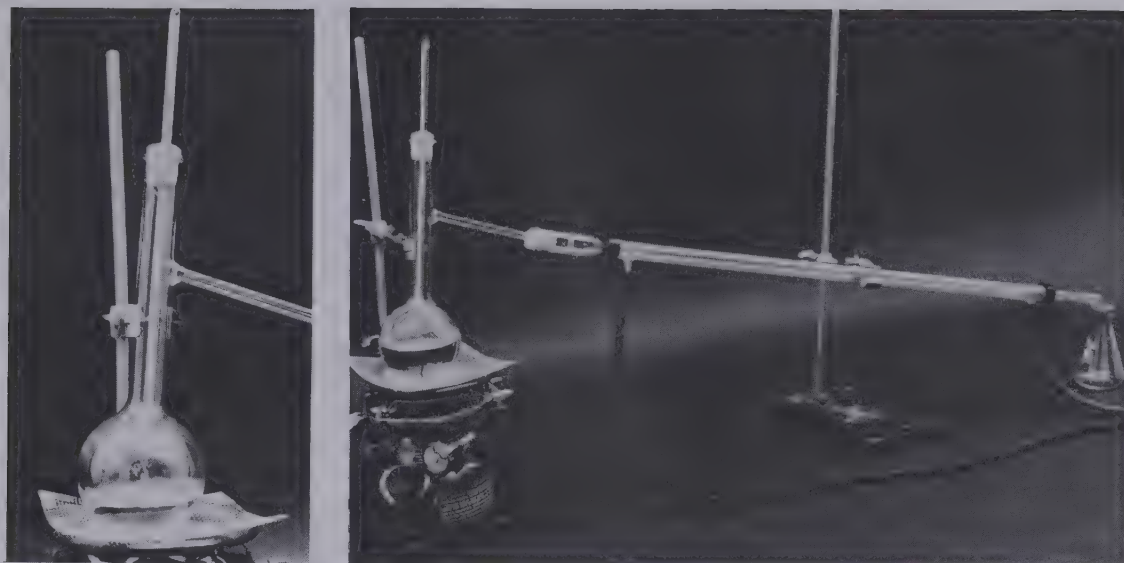
Interpretation of a sensory message.

Prediction

Observation of facts and attempts to interpret them enable us to make reasonable predictions about what may or may not be true. Imagination and experience help us to make good predictions. An inference that can be tested by an experiment is called a *hypothesis*; this word means an explanation that can be tested.

For example, if you infer that your dog has barked at a prowler, and can think of a test to see if that explanation of his barking is true or not, you have a hypothesis: "I infer that the dog barked because a prowler was nearby. I will test this by inviting a friend that the dog does not know to come around after dark some evening." That would be a good way to test your hypothesis; it might also cost you a friend.

Notice that an inference is always based upon observation (the dog barked) followed by an explanation (because there was a prowler). Then, if you can think of a test (ask a friend to come over late some dark night), your inference is called a *hypothesis*. *An inference is a hypothesis if it meets two criteria: (1) it is based upon observation and (2) it is testable.*



The apparatus used for a laboratory distillation of a liquid.

Experimentation and Investigation

To be of any scientific value, an inference must be testable. Otherwise, we can never tell if it is true or false. Testing involves investigation: invite someone over and tell him to act like a prowler. Investigations in chemistry are usually carried out in the laboratory and are called *experiments*.

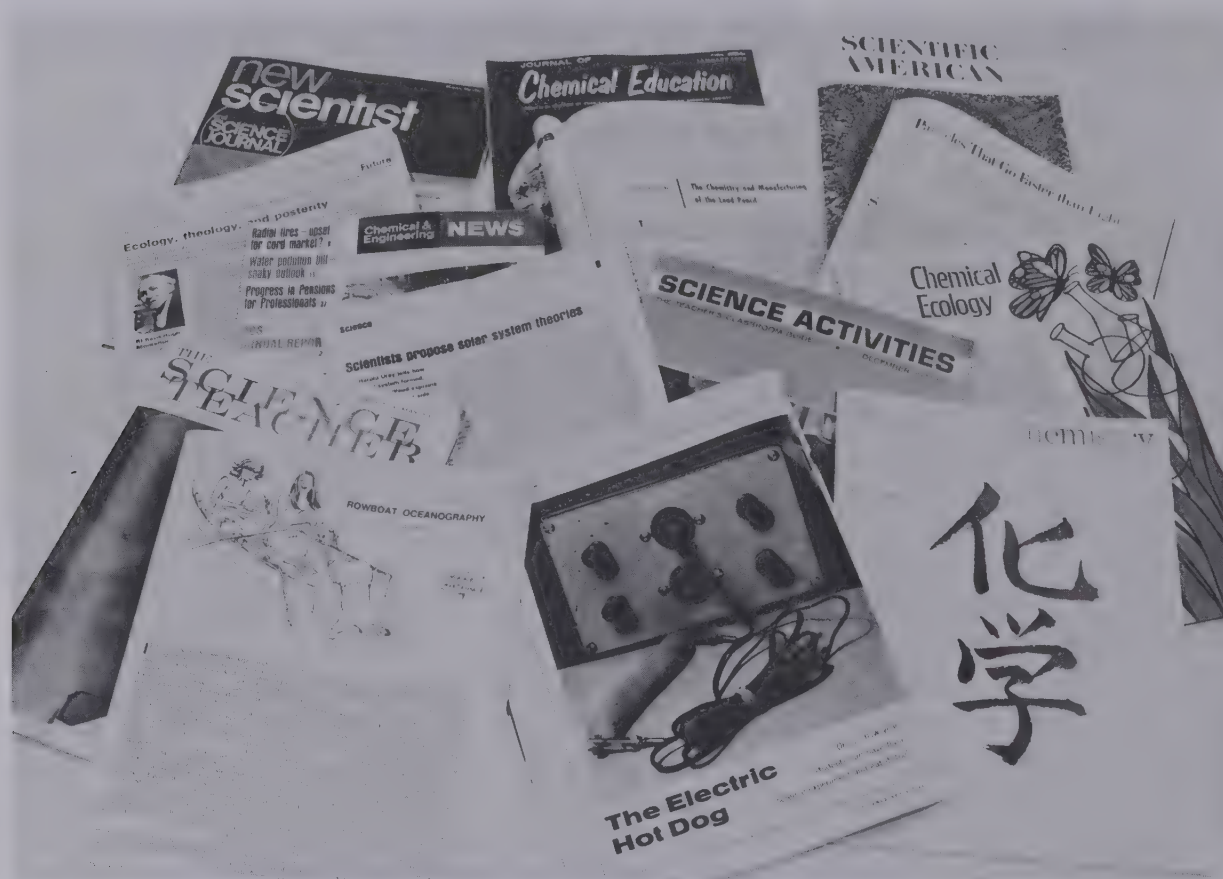
Experiments must be designed in such a way that we can expect to make new observations that will help us evaluate our hypothesis. For example, we would want to be sure that the dog is in good health. If the dog were sick, he might not be able to bark loud enough for us to observe his barking. We would want to be sure that our friend was dependable and would arrive at the time decided upon. We might want to stand guard ourselves, to be sure that the real prowler (if there is one) did not return and take off with the dog.

An investigation must be planned with care so that the observations we make are meaningful. *The conditions must be controlled so that the investigator knows what is producing the new observations he notices.* Often in science, this requires the development of new equipment or clever applications of old ideas which have never been used before. Suppose, for instance, that you do not wish your dog to attack your friend when you make the investigation about the possible prowler. How would you change the plans? Tying up the dog probably would not work, if your dog also barks because he is tied. Think of an innovative way to carry out your test.

It would not do, ordinarily, in any important test, to be satisfied with only one trial. The investigation or experiment should be repeated, perhaps hundreds of times, for a thorough scientific experiment. In such cases, what is learned on the first few tests is refined and more precise observations are made in the next series of tests. How many times did the dog bark? Does he bark more loudly when first aroused, or later as the "prowler" comes closer? What if it is raining? Does the amount of rain make any difference? What inferences

can be made because the dog barks loudest (if he does) when the “prowler” is further away? Why does he not bark at all (let us suppose) when it rains? These new explanations of the more detailed observations would help us think of a better, more reliable, hypothesis. *Since we can never make a perfect investigation, even our best hypothesis would not be known to be perfectly true.*

Scientists may perform an experiment hundreds of times in order to refine their procedures and to obtain more precise information. Each time the cycle begins again: observation, interpretation, inference, construction of a more complete hypothesis based upon reasoning and experience, and then more testing. No hypothesis is ever completely proved. In fact, we seldom “prove” anything in science. *The best we can do is to conclude that in the light of our careful observations, a hypothesis appears to be true.*



Some of the publications used to communicate scientific information.

Communication

The most brilliant experiment ever performed would be of little value if no one ever heard about it. Therefore, communication is of utmost importance in science. When a scientist feels his work is as precise and as complete as he can make it, he publishes the results of his experimentation. This has several benefits. It allows other scientists to try to duplicate his work and either confirm or dispute his conclusions. If his findings are confirmed by others, confi-

dence in his hypothesis grows and scientific knowledge increases. If his hypothesis is found to be untrue, then other investigators do not have to spend time working on it and scientific knowledge is again increased. *It is just as important to learn, through testing, that an idea is false as to find that it is probably true.* The scientist seeks to learn the truth as much as possible; he is willing to reject ideas when the evidence shows that his idea is false.

Many of the laboratory activities in which you will engage will not be experiments in the sense that you will discover new knowledge, although quite often these discoveries will be new to you. This will enable you to experience a sense of exhilaration and accomplishment yourself. It is most important that you acquire the procedures of the practicing scientist. You are encouraged to exercise your imagination, to utilize all your senses, to become a good observer, and to gain skill in making inferences and in formulating and testing hypotheses.

You are expected to keep complete and accurate records of your laboratory experiments and to report your findings in the accepted manner. You will be given the opportunity to plan experiments to test hypotheses which you yourself propose. To do so means that you must acquire a new vocabulary, develop skill in making precise measurements and become familiar with problem-solving techniques. This can be the most rewarding part of your study of chemistry, for you will be engaging in the procedures of the scientist.

1-3 • THE CONCEPT OF MATTER

Since the science of chemistry is primarily concerned with matter and the changes it undergoes, we need to know what matter is. *All material which has substance and takes up space is matter.* It can exist in three forms: solid, liquid, and gas. These forms are known as states of matter. We are most familiar with water in its liquid form, but we know that it also occurs in a solid state (ice) and in a gaseous state (water vapor).



The shapes of solids, liquids, and gases.

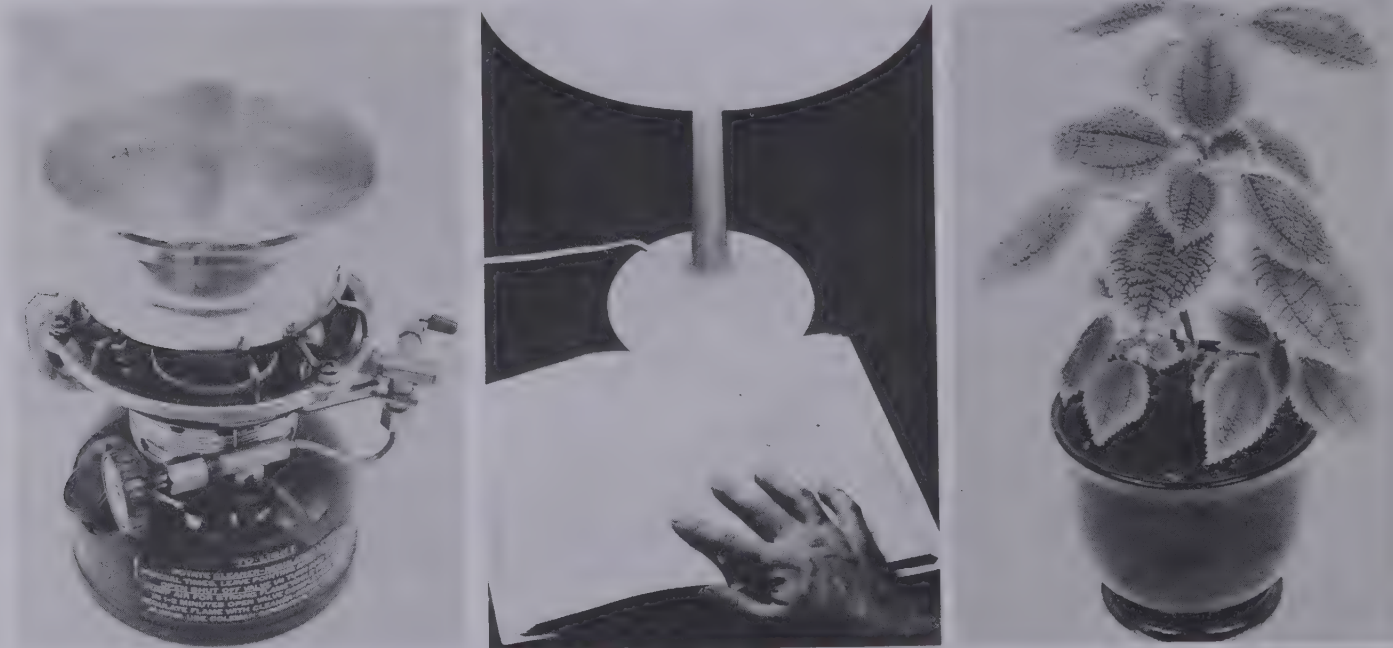
Solids are characterized by fixed shape and definite volume. A brick remains in a definite shape and retains a certain volume under normal treatment. A great amount of force is needed to change the shape of a brick. So it is with all solids, though not as much force is required for some; a piece of solid cheese or rubber can be squashed between your hands.

Liquids are characterized by definite volume, but their shape depends entirely upon the shape of their container. Pressure does not decrease the volume of a liquid to any appreciable extent. All liquids tend to evaporate, or to change into the gaseous state. Some do this more readily than others. For example, alcohol evaporates much faster than oil at the same temperature. A property of liquids related to the rate at which they change to a gas is known as *vapor pressure*. The higher the vapor pressure, the more readily a liquid evaporates. We will consider this in greater detail in our study of liquids.

Gases have no definite shape or definite volume. Gases take the shape of their container and will occupy all the space that is available to them. Remember when you were younger and blew up a balloon shaped like an animal's head? The air, the gas you blew in, took the shape of the balloon and filled it. Pressure has a great effect upon the volume of gases, whereas it has practically no effect upon the volume of solids or liquids.

1-4 • THE CONCEPT OF ENERGY

We cannot speak of changes in the states of matter without giving attention to the energy relationships that cause these changes. Energy is difficult to define because it occurs in many forms. We have heat energy, light energy, electrical energy, chemical energy, mechanical energy, and others. Energy can be changed from one form into another. The mechanical energy of falling water can be changed into electrical energy by a generator. Electrical energy can be changed into light and heat energy. We can begin to define energy by



How is energy involved in these three situations?

saying that it is a quality associated with all matter, which can be converted into work under the proper conditions. For example, the chemical energy of burning fuel does work in moving an automobile.

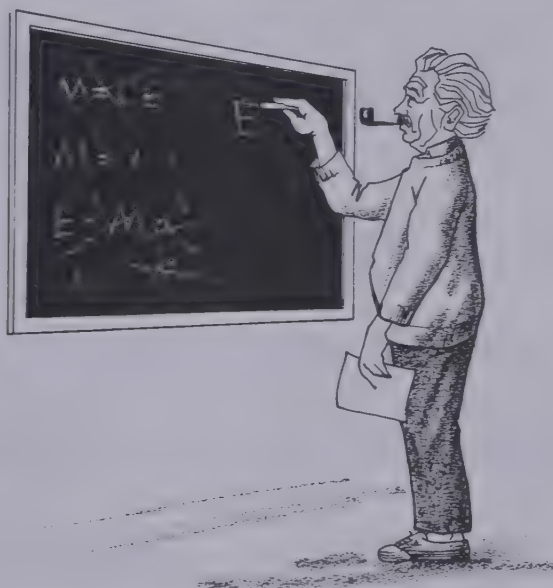
Matter cannot be changed from one state into another unless energy is absorbed or released. When liquid water changes into ice, heat energy is released. This is an *exothermic* change. Conversely, when ice is changed into water, heat is absorbed. This is an *endothermic* change. You will encounter more exothermic than endothermic changes as you study *Keys to Chemistry*. When wood burns, both heat and light energy are released as the carbon and hydrogen in the wood unite with oxygen from the air to produce carbon dioxide and water. This chemical change is exothermic. In our laboratory experiences we will investigate many kinds of reactions in which matter and energy are interrelated.

1-5 · THE RELATIONSHIP BETWEEN MATTER AND ENERGY

Scientists have long known that matter can be changed from one form of matter into another, and that *the total amount of matter involved in the change remains constant*. This came to be known as the Law of Conservation of Matter.

Likewise, energy can be changed from one form into another, and *the total amount of energy involved remains constant*. This came to be known as the Law of Conservation of Energy.

Albert Einstein was the first to suggest that, under certain conditions, matter and energy are equivalent. Under special circumstances, matter and energy can be transformed one into the other. He expressed this relationship in the equation: $E = mc^2$, where E is energy, m is mass, and c is the speed of light. This means that the law of conservation of matter and the law of conservation of energy are really one law. Since the work of Einstein, we state the new concept as the Law of Conservation of Mass-Energy.



How did Einstein arrive at his famous equation?

The change of energy into matter or of matter into energy in ordinary chemical reactions is too small to be detected in conventional measurements. So, in our experimental work we will use the separate laws of conservation of matter and of energy.

1-6 • MEASUREMENT OF MATTER

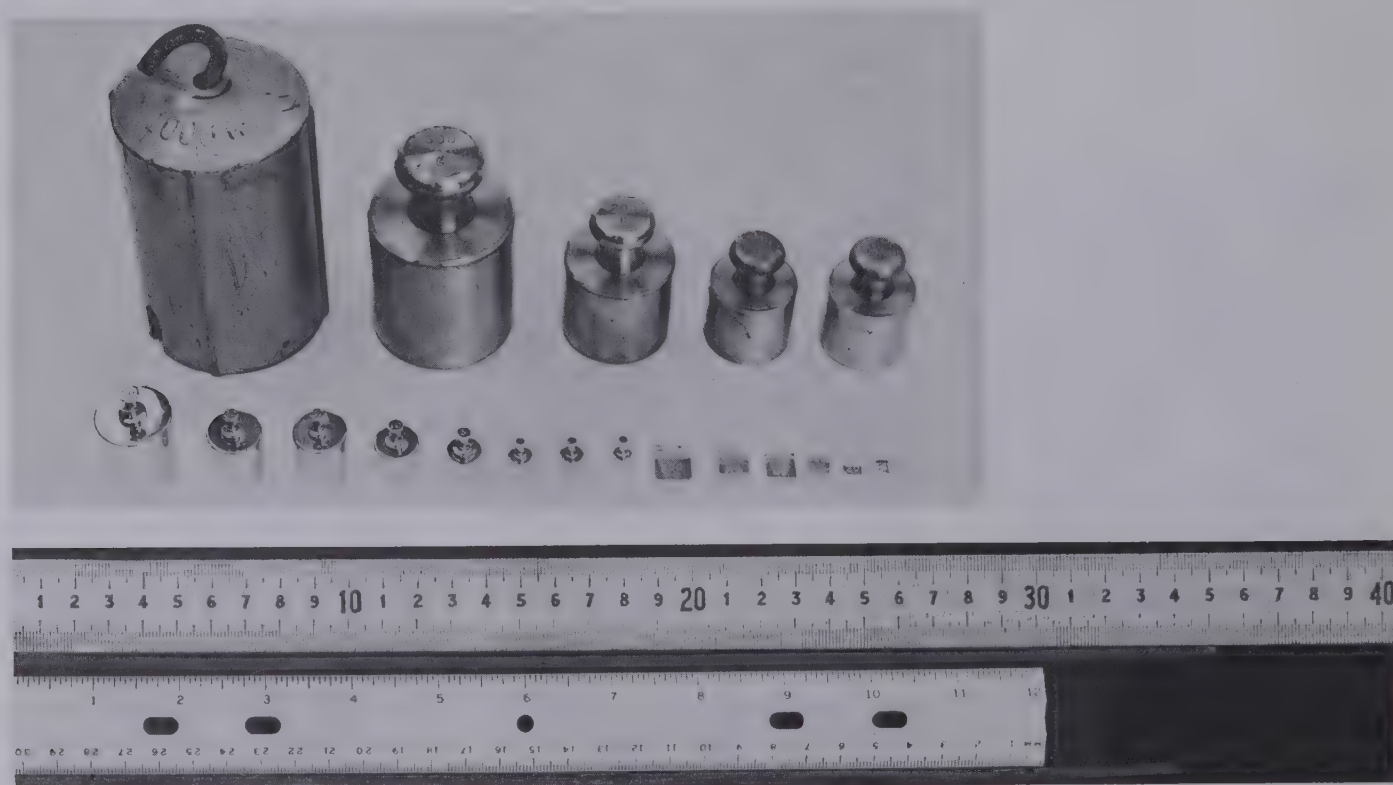
Measurement is important in science because it helps us to obtain quantitative information. In chemistry we are especially interested in measuring length, mass, time, and temperature. From length measurements we can derive volume.

Systems of Measurement

The English system of measurement is the one commonly used in the United States and Canada. In this system the foot is the fundamental unit of length, the pound is the fundamental unit of weight, and the second is the fundamental unit of time. This system is not very satisfactory for scientific work.

The system of measurement used by scientists is called the International System of Units. It is a decimal system, similar to the system of counting money in the United States and Canada. For example, as you know, \$1.32 is the same as 132¢; to change from dollars to cents, move the decimal point two places to the right.

In round figures the straight-line distance between the North American capitals, Ottawa and Washington, is 750,000 meters. This is the same as



How does the centimeter compare with the inch?

750 kilometers. You move the decimal point three places to change from kilometers to meters. (The distance between Ottawa and Washington is also approximately 455 miles; try converting this to yards!) The International System of Units is easier to use.

Instead of inches, use centimeters. (The diameter of a nickel is about 2 centimeters, or 2 cm.) Instead of miles, use kilometers. (Roughly, 3 km is about 2 mi.) Instead of yards, use meters. (They are almost the same.) Instead of feet, you could use decimeters, but a decimeter is only about 4 inches, so nobody bothers.

Instead of quarts, use liters. (They are almost the same.) The International System of Units has no equivalent for cups and pints; volumes smaller than a liter are measured in milliliters. Half a liter, called 500 milliliters (because 1000 milliliters make one liter), is approximately one pint. The International System of Units has no equivalent volume for gallons; you would just say "Four liters please" if you really wanted to get about a gallon.

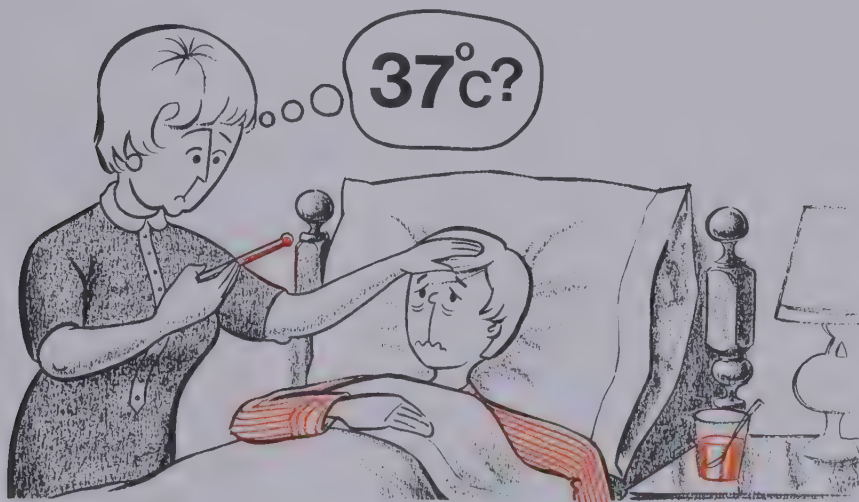
Instead of pounds and ounces, the International System of Units uses kilograms and grams. (A one-kilogram object weighs a little over two pounds.) The gram is quite small compared to the ounce; there are about 30 grams in an ounce.

The unit of time in the International System of Units is the same as in the English system: the basic unit is the second, and there are 60 seconds in one minute, 60 minutes per hour, 24 hours a day. As you can see, the time units are not decimalized.

The International System of Units also has a special temperature scale, called the Celsius scale, or degrees C. The Celsius scale is based upon the freezing point of water under special conditions. This point, called the triple point of water, is at 0.01°C , just a shade above the ordinary freezing point of water, 0°C .

Another special temperature on the Celsius scale is the boiling point of water, which is defined as 100°C . So, on the Celsius scale of temperature there are one hundred degrees between the freezing and boiling points of water. (The Celsius scale used to be called the centigrade scale.) The freezing point is 32° on the Fahrenheit scale that you already know; 70°F is about 21°C .

Is the patient running a fever?



So, the fundamental units are: length, the meter; volume, the liter; mass, the gram; and time, the second. To talk about larger or smaller amounts, prefixes are used: kilo- (one thousand); centi- (one hundredth). There are 1000 grams in one kilogram; a meter contains 100 centimeters.

For centi- we divide. (Notice that the prefix centi- ends with the letter *i*.) A meter is divided into 100 centimeters. Millimeters are even smaller; a meter is divided into 1000 millimeters. It requires 1000 milligrams to make one gram and 1000 milliliters to make one liter. (Note the *i* at the end of milli-.)

Kilo- is a prefix that also signifies 1000 (but it does not end with *i*). Kilo implies multiplication. If you have a kilogram, you have 1000 grams. A kilometer is 1000 times longer than a meter.

Here are seven of the prefixes in the International System of Units with the most frequently used ones indicated in bold face type:

<i>Prefix</i>	<i>Meaning</i>
mega-	$1,000,000 \times \text{unit}$
kilo-	$1,000 \times \text{unit}$
hecto-	$100 \times \text{unit}$
deca-	$10 \times \text{unit}$
deci-	unit divided by 10
centi-	unit divided by 100
milli-	unit divided by 1000

The units are gram, meter, and liter.

Brief History of the International System of Units

The general idea of using a decimal method for measurement became popular in France at about the time of the French Revolution (1789–1792). After the revolution things were in a mess, generally speaking. It was a good time for cleaning up all sorts of past mistakes, including the confused system of measurement in use before the revolution. It was decided the new system should be based upon a natural object, as before, when a “foot” was the length of the King’s foot, and a “yard” was the distance from his nose to the end of his middle finger when he stretched out his arm. With no more kings, a new standard was needed. The standard selected was one ten-millionth of the distance from the earth’s equator to the North Pole. The trouble was that the location of the North Pole could not then be determined precisely. So, a mistake was made, and the length, one meter, is not quite one ten-millionth of that distance. Today we have a new standard, based on the wavelength of a certain color of light.

You have often seen red neon signs. Neon is a gas. Another gas, quite similar to neon, is krypton. If someone made a krypton sign, it too would be red when it was turned on, but the red color would be a different shade of red. The wavelength of this red color is the basis for the meter today. (It doesn’t make any difference to know it, but one meter is 1,650,763.73 times longer than the wavelength of that special red color.)

For volume, someone suggested a cubic meter (which is equal to 1.31 cubic yards). This idea was rejected because the unit was too large. Instead, a cubic decimeter, or liter, was chosen. It is just a little larger than one U.S. quart.

For mass, the gram was chosen as the mass of one cubic centimeter of water at 4° Celsius, a temperature slightly above freezing.

Measurement of Mass

One universal property of matter is *inertia*. This is the property that causes an object to resist change in the direction or rate of motion. Inertia causes you to push against the seat back when an automobile or airplane accelerates rapidly. When a fast-moving automobile makes a sharp turn, inertia causes you to be thrown against the side of the car opposite from the direction of the turn. You tend to keep on going in the same direction at the same rate.

To measure the inertia of matter is not practical. Therefore, we normally use weight as a measure of the mass of an object. *Mass is the quantity of matter in an object* and, for a given object, does not change anywhere in the universe. *Weight is a force*. It is a measure of the earth's gravitational attraction for an object. Weight varies with the distance from the center of earth. Since earth is not a perfect sphere, the force of gravity varies from one location to another on earth's surface. Although your mass would be the same, your weight is less on the top of a mountain than when you are at the sea shore. Unfortunately, this effect cannot be applied in a practical way by overweight (really, overmass) people who wish to relax on the beach, since mass doesn't change with location.

That is, there is a difference between mass and weight, but even on the highest mountains, compared to any sea shore, the change in weight is small, and the mass remains the same in both locations. So, for our current purposes, we can use the terms mass and weight interchangeably. As a student of science, however, you should understand that *mass and weight are not the same*.

1-7. MEASUREMENT OF TEMPERATURE AND HEAT

Temperature is a measure of the energy of motion of the particles in matter. Energy of motion depends on two things, the mass of the moving object and its speed. The higher the temperature, the faster the particles are moving. When heat energy is applied to matter and the temperature rises, we can say that the speed of the particles has increased. Temperature is one measure of *the effect of heat upon matter*.

Heat energy normally passes from an object at a higher temperature to one at a lower temperature. Ice feels cold to touch because heat energy passes from your fingers, which are at a higher temperature, to the ice, which is at a lower temperature. A hot iron feels hot for the opposite reason. Thus, temperature is a quality which we can use to determine the direction of heat flow.

Many substances expand as their temperature rises. We take advantage

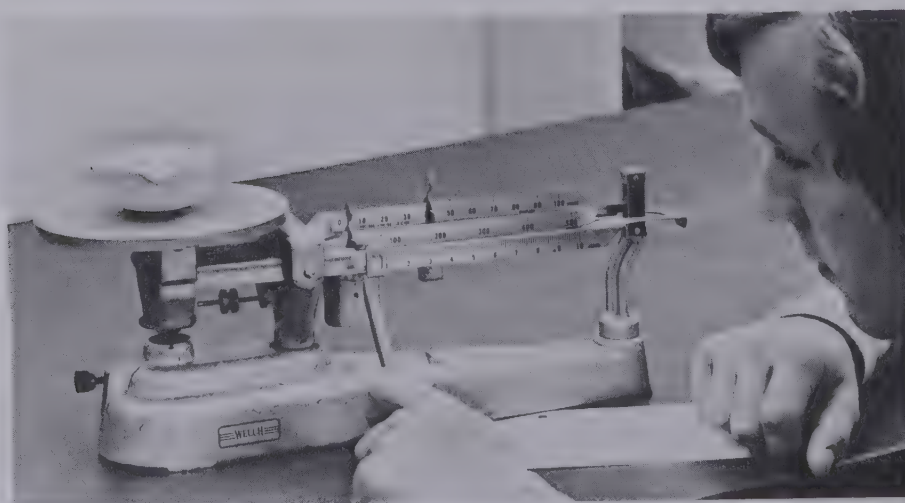
of this as a way to measure temperature. The liquid in a thermometer expands as it gets hotter and contracts as it cools. The result is a change in length of the liquid column along a marked scale. As you have learned, the Celsius scale is designed so the top of the liquid is at zero when the thermometer is at the temperature of freezing water, or melting ice, and at 100 when the thermometer is at the temperature of boiling water (when the atmospheric pressure is normal). The space between is divided into 100 equal spaces, and more of the same-sized spaces are also marked off above the 100 mark and below the zero mark.

Quantities of heat are measured in calories. One calorie is defined as the heat needed to raise the temperature of one gram of water one degree Celsius. When a match is burned, about 800 calories of heat are released. When one teaspoon of sugar is burned, about 15,000 calories (15 kilocalories) of heat are released. Most diet watchers have learned that there are about 15 calories in one teaspoon of sugar. These are "diet calories"; a diet calorie and the scientific kilocalorie are the same.

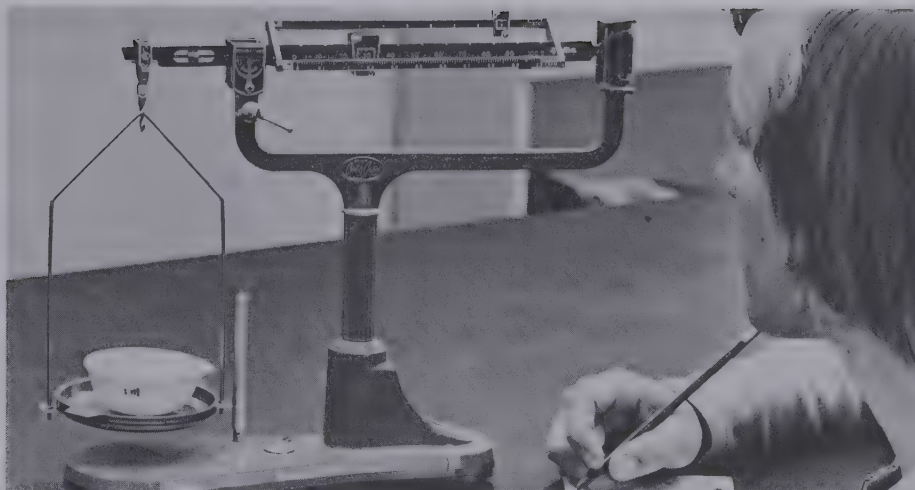
1-8. UNCERTAINTY IN MEASUREMENT

There is some uncertainty in every measurement. This uncertainty has two major sources: (1) the limitations of the instrument and (2) the skill of the observer in using the instrument. Human error is often greater than that built into the instrument. Poor eyesight, careless reading of scales, and lack of understanding of how to use the instrument may contribute to unreliable data. However, such factors as misreading numbers, improper use of instruments, and errors in calculations are classed as blunders. These can be avoided by learning to be a careful worker.

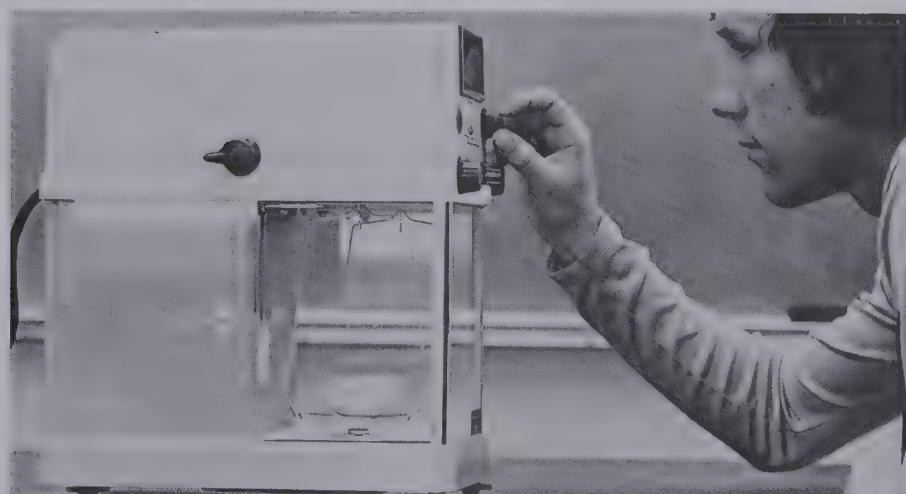
We cannot control the sources of uncertainty which are an inherent part of the measuring instrument. In order to keep costs low, most measuring devices are mass-produced by machine. The greater the precision of the instrument, the more carefully it has to be made and, therefore, the greater the cost.



The scale reading is 40.5 grams.



The scale reading is 39.97 grams.



The scale reading is 39.8984 grams.

(The same object is on all three balances.)

You can purchase a plastic rule for a few cents, whereas a more carefully machined linear measuring device, such as a micrometer, may cost as much as fifty dollars. Graduated cylinders that are mass-produced may not be uniform in diameter, thus introducing greater uncertainty into volume measurement than a more carefully made instrument such as a graduated pipette. The point to remember in choosing an instrument is whether it is suitable for the purpose of the measurement. If you wish to know only the approximate length of a room, a meter stick will serve very well. If you need to know the thickness of aluminum foil, the meter stick is of little use; a more precise instrument would be required.

Limit of Precision

Assuming that the experimenter understands the proper use of a measuring device and uses it with skill, the limit of precision for any measurement is

determined by the instrument itself. For example, here is a centimeter scale:



Use this scale like a ruler to measure the diameter of a dime. Put the dime on the marked scale and determine its diameter. You can see that the diameter is more than 1 cm and less than 2 cm. The idea is to estimate how much more than 1 cm. A good guess is 1.7 cm; another good guess would be 1.6 cm, or 1.9 cm. The limit of precision is such that we cannot be sure within 0.1 or 0.2 cm. We can be sure only of the 1 in all of the numbers: 1.6, 1.7, 1.9. Our limit of precision is determined by the measuring instrument we used, the centimeter scale.

Here is a more refined scale, with both centimeters and millimeters marked on it. Only the centimeters are numbered, since the millimeters are so small that their numbers would be either too tiny to see clearly, or too large to fit the space.



Measure the diameter of a dime with this scale. You might get 18 mm, or maybe 17 mm, but this is not good enough. With a more precise scale, we must be more observant. The last digit should be estimated, and neither the 7 in 17 nor the 8 in 18 is estimated. Try again. How about 17.8 or maybe 17.9 mm? The .8 or .9 are guesses, or estimates. There is no way to tell for sure which of them is closer to being correct. Our limit of precision is now plus or minus about 0.1 mm. We have improved the precision by using a better measuring scale.

Normally, in all scientific measurements, we include one estimated, or guessed at, digit. Other experimenters may disagree with the estimated digit; however, all will agree with the digits we obtained from the scale itself if we have read the scale carefully. As you make measurements, be sure to make the last recorded number on the right your estimated number.

It doesn't sound very scientific to make guesses, but it really can be. Notice that in order to make the best guess we can, we had to be very sure about the other numbers, the ones that were not guessed at. It is very scientific to *be as precise as you can with measurements*.

Precision and Accuracy in Measurement

Most dictionaries define precision and accuracy as almost synonymous, but these words have quite definite, and different, meanings to a scientist. *Precision is how closely two measurements of the same thing agree*, when both measurements are made with equal care by the same measuring instrument.

For example, when we used the rather poor centimeter scale, the diameter of a dime was found to be 1.6, 1.7, and 1.9 cm. This agreement was good, but not especially close. The range of agreement was 0.3 cm (from 1.6, the smallest, to 1.9, the largest).

Accuracy is how close a measurement is to an accepted standard. According to the U. S. mint, a U. S. dime has a diameter of 1.780 cm. So, none of our measurements was particularly accurate, although some were pretty close.

When we used the better scale, the precision was improved: all the measurements were closer to each other: 1.78 and 1.79 cm (this is the same as 17.8 and 17.9 mm; remember, move the decimal point when changing from mm to cm). The precision was 0.01 cm in this case. Accuracy was improved also; the results both came closer to the standard value of 1.780 cm.

Accuracy is expressed in terms of error, how much the measurement is off, in two ways: (1) experimental error and (2) percentage error. To determine the experimental error, we take the difference between the measured value and the standard value.

Let us use our examples to show this:

Measured value for the diameter of a dime: 1.78 cm

Standard value for the diameter of a dime: 1.780 cm

Experimental error: $1.78 \text{ cm} - 1.780 \text{ cm} = 0.00 \text{ cm}$. For the other measurement:

Measured value: 1.79 cm

Standard value: 1.780 cm

Experimental error: $1.79 \text{ cm} - 1.780 \text{ cm} = 0.01 \text{ cm}$.

The experimental error must always be labeled in the same units as the measured and the standard values. Whether you subtract a large number from a small one or whether you take the small value from the large is not important here. If you wish to retain a plus or minus sign on the experimental error value, it will, however, tell you whether your measurement was greater or smaller than the standard value.

Percentage error is useful, because it describes the size of the error. Percentage error is calculated by these steps:

1. Find the difference between the measured value and the standard value (this is the experimental error).
2. Divide the experimental error by the standard value.
3. Multiply the quotient obtained in step 2 by 100% (so the answer will be expressed as a percent).

As an example we can calculate the percentage error for the 1.79 cm diameter measurement of the dime.

1. Measured value – standard value (or, if you don't care whether your answer shows the direction of the experimental error, the other way around):

$$1.79 \text{ cm} - 1.780 \text{ cm} = 0.01 \text{ cm}$$

2. Experimental error divided by the standard value:

$$\frac{0.01 \text{ cm}}{1.780 \text{ cm}} = 0.0056$$

3. Quotient from step 2 multiplied by 100%:

$$0.0056 \times 100\% = 0.56\% \text{ error}$$

The consideration of error is important, because it is an indication of how carefully you have performed an experiment. You should strive to keep your percentage error as small as possible. The percent allowed will vary with the kind of experiment you do.

Significant Figures

Actually, you have already learned the basic rule of the method of significant figures: whenever you take a measurement, be as careful as you can, and estimate one more number than the instrument can clearly establish.

If you follow this rule, you will be writing down measurements in which all the numbers are significant figures. For example, suppose the diameter of a quarter was measured to be 2.4265981 cm. We would conclude that a very good measuring instrument had been used, or that the person making the measurement did not know the basic rule for the use of significant figures. Using the best scale printed in this chapter, we might get 2.42 or 2.40 cm. We are sure of the first 2 and the 4, but the last digit, the 2 or the 0, is an estimate.

Often, it will be necessary to multiply, divide, add, or subtract numbers obtained from measurements. When we do this kind of arithmetic, more rules apply to the method of significant figures. These are explained in Appendix 3 of this book.

1-9. VARIABLES AND EXPERIMENTATION

If you already know how to make graphs from data tables, and if you know how to recognize a linear relationship and tell the difference between linear relationships when you see two graphs, check your ability by doing Practice Exercise 8 at the end of the chapter. If you do well, you may skip the discussion which follows. If not, this discussion is for you.

Generally, in performing an experiment we cause one factor to change and observe the effect on a second factor. The factors in an experiment which change are called *variables*. If the results of an experiment are to be meaningful, we must be careful to change only one variable at a time. Otherwise, we cannot be certain which variable is responsible for our observations. A *controlled experiment* is one in which only one factor at a time is changed.

Dependent and Independent Variables

Suppose we set up a controlled experiment to determine the effect upon a student's mass if he eats candy bars regularly. Each day we will give him the same thing for breakfast that he had on the first day. His lunches will be the same, and his dinners, too. We will have him exercise the same way each day, twenty push-ups and jogging for three miles, perhaps. In addition, we will feed him candy bars and keep track of his mass.

The data we collect might look something like the values recorded in Table 1.

Mass of Student vs. Candy Bars Eaten	
Total Number of Candy Bars Eaten	Mass of Student in Kilograms
0	43.0
2	41.5
4	39.1
7	38.8
10	37.0
12	34.5
14	34.5
16	31.9
17	34.0
19	35.0
23	42.2
25	44.6
29	50.3
32	53.2
36	60.0
38	61.7
40	66.0
44	69.5
47	75.0
49	78.7
53	82.0
56	87.1
59	91.8



Table 1-1

Notice that in our data table there are two columns; the left column is the total number of candy bars, the variable that we controlled. It is called the *independent variable*. The number of candy bars affected the student's mass; his mass depended upon how many candy bars he had eaten. So his mass is the *dependent variable*; its value depends upon the independent variable.

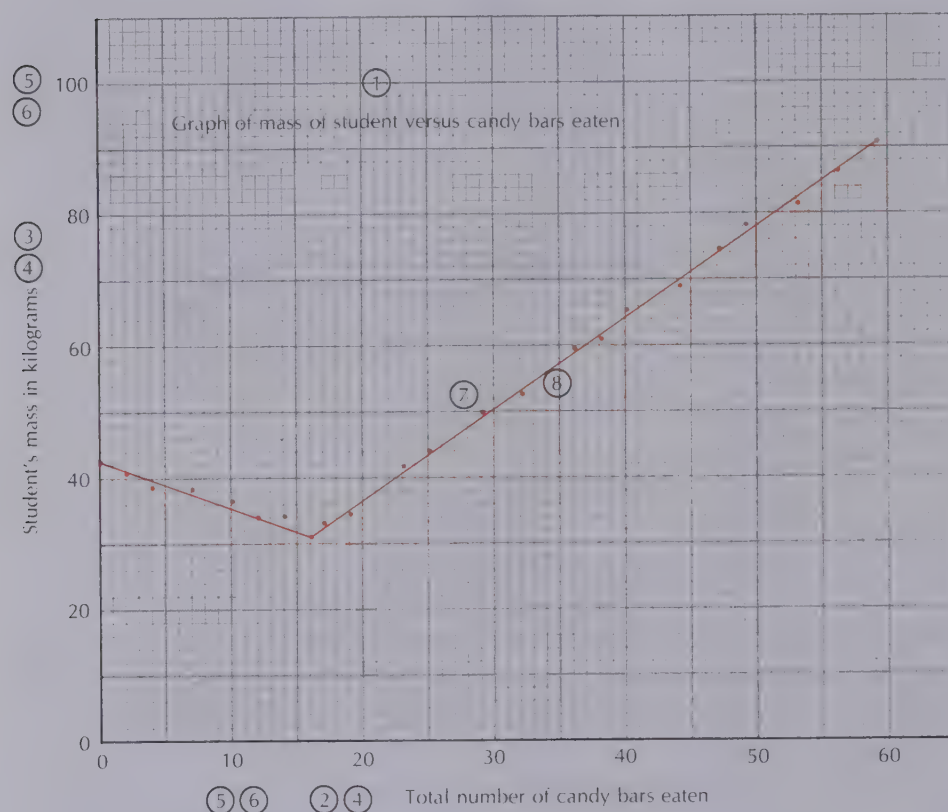
Each different number of total candy bars eaten is associated with a particular mass. The associated number of candy bars and number of kilograms form a pair of values; we call these *ordered pairs*.

Graphing Ordered Pairs

The relationship existing between variables can be seen more clearly if we plot a graph of the ordered pairs. Rules for graphing are:

1. Place a title on the graph.
2. The *independent variable* is always plotted on the horizontal axis, known as the x-axis. This is called the *run* on a graph.

3. The dependent variable is always plotted on the vertical axis, known as the y-axis. This is called the *rise* on a graph.
4. Each axis must be labeled according to the variable it represents.
5. Each axis must be marked in equal intervals, or units. The units should be planned so that the graph is large enough to be easily read.
6. The scale of units may be different for each axis, but must be clearly indicated.
7. Each point on the graph is marked with a dot.
8. After all points have been marked, a "smooth" line should be drawn which is as close as possible to most of the points. It is highly unlikely that every point will lie on this line, because of experimental uncertainty. However, if the measurements have been made carefully, most points should fall very near to the line, and some will be on the line.



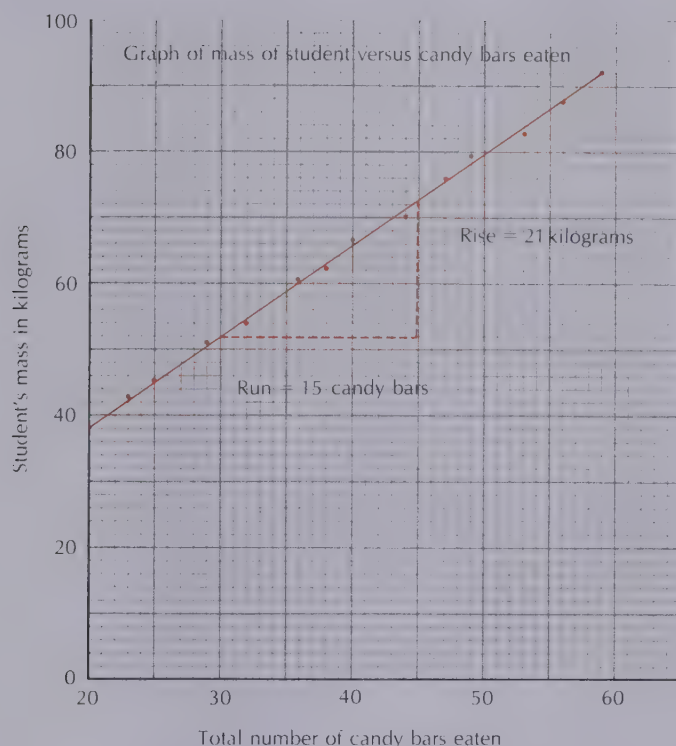
This is a graph of the student candy-bar eater's mass plotted against the number of candy bars eaten. The numbers on the graph refer to the rules given in Sec. 1-9 for preparing a meaningful graph.

1-10 • LINEAR RELATIONSHIPS

Experimental data obtained in the laboratory should be recorded in a table so that it is easily read. Many times, when dealing with two variables, it is helpful to graph the data in order to establish a mathematical relationship between the variables. If the graph is a straight line, we have a linear relationship. In the case of the student's mass before and after eating the sixteenth candy bar, we have a decreasing linear relationship followed by an increasing one. This means that as the number of candy bars eaten increased, the student's mass at first decreased in direct proportion, and later, after the sixteenth candy bar, increased in direct proportion.

The Slope of the Line (Proportion)

Let us look at the graph of the student's mass vs. the number of candy bars eaten, from candy bar number 20 on. We can see that as the candy bars are eaten, the student gains weight. The data table of ordered pairs contains the same information but requires longer to interpret. But the graph is even more meaningful since we can determine *how much* the student's mass increases for each candy bar he eats. This is done by finding the slope of the line, which is simply a measure of how steep the line is.



Hills and stairways vary in steepness. If you have been in mountainous country, you may have seen a road sign which read, "Steep grade ahead." This means that the number of feet of vertical rise for each mile of road travelled is fairly great. In other words, to find how steep a hill is, we divide rise by run. This is also true for linear relationships on a graph.

Look at the graph and note that the rise units must be counted in the same scale as the vertical axis, which in this case is 2 kilograms per horizontal line. The run units must be counted in the same scale as the horizontal axis, which in this case is 1 candy bar per vertical line. The slope of the line may be found by dividing the rise by the run for *any two points on the line*. In the graph given, the slope is found to be 1.4 kilograms per candy bar. This means that for every candy bar eaten, the student increases in mass by 1.4 kilograms.

Notice that, because the linear relationship between the two variables is shown on the graph by a smooth line, rather than a zigzag line, the line

passes near, but not through, all of the dots. The two pairs of points we used to compute the slope of the graphed line are slightly different from the actual observed points listed in the data table.

When the graph of two variables is a straight line, we may divide the rise by the run for any two points on the line and always get the same quotient. This constant quotient is called the proportionality constant, m , and equals the slope of the line. The mathematical equation for a straight-line graph which passes through the origin is $y = mx$, where y is the dependent variable (on the vertical axis) and x is the independent variable (on the horizontal axis). In this special case, the two variables are said to be in *direct proportion*. In cases like our example, in which the line does not pass through the origin, the equation is $y = mx + b$, where b is the value of y when x equals zero.

1-11. CONCEPT OF DENSITY

Density of matter has to do with *how much material is in one unit of space or volume*. The one unit of space can be anything. For example, the space inside one cigar box could be considered one unit of space.



If we put ten marbles in the one space inside a cigar box, the density would be ten marbles per one cigar-box-space. The box is the unit. Unless the marbles were very large, we could get more marbles in. Suppose we added some more, until we had 23 marbles inside the cigar-box-space. Then the density would be 23 marbles per one cigar-box-space.

When used by scientists, density involves the mass (of the marbles) instead of the number. Also, scientists would use a volume of one space in the International System of Units, such as one liter or one cubic centimeter, instead of one cigar box.

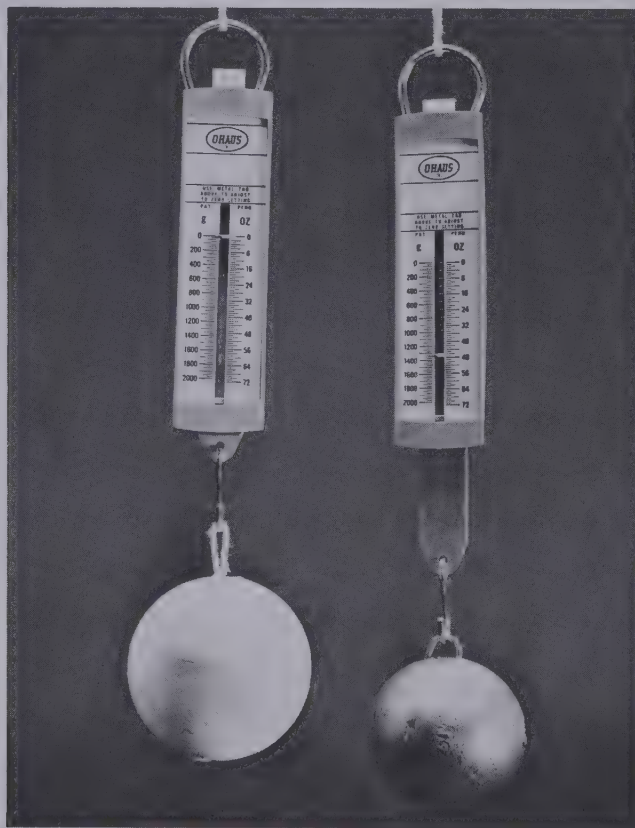
Three pennies have a mass of 9.3 grams (9.3 g) and a volume of a little bit more than one cubic centimeter (cc). The amount of copper in 1 cc of copper is 8.9 g. So, the density of copper is 8.9 g per cc, or 8.9 g/cc.

The amount of iron in 1 cc weighs 7.8 g, so the density of iron is 7.8 g per cc. In fact, you can tell whether a coin is made of iron or copper by determining its density in the laboratory.

For example, some very old Roman coins were made of iron. Such a coin might have had a mass of 49.14 g and a volume of about 6.3 cc. So, its density could be found by dividing:

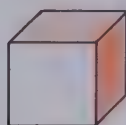
$$\frac{49.14 \text{ g}}{6.3 \text{ cc}} = \frac{7.8 \text{ g}}{1 \text{ cc}}, \text{ or } 7.8 \text{ g/cc}$$

We get 7.8 g/cc, as we expected, since we already knew it was made of iron.

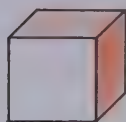


What causes the variation in density from one material to another?

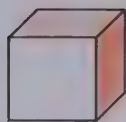
We will consider density to be the amount of mass in one cubic centimeter. Each different substance has a different mass in one cubic centimeter. By using density, we compare the mass of one cubic centimeter of any substance with that of any other substance. We can compare iron with copper, or with lead. We can compare feathers with sand. The old riddle Which weighs more, a ton of feathers or a ton of sand? is an example. They both weigh the same, but the density of feathers is a lot less than the density of sand, so a ton of feathers would make a very big package compared to a ton of sand. Equal masses of different substances (substances with different densities) occupy proportionately different volumes.



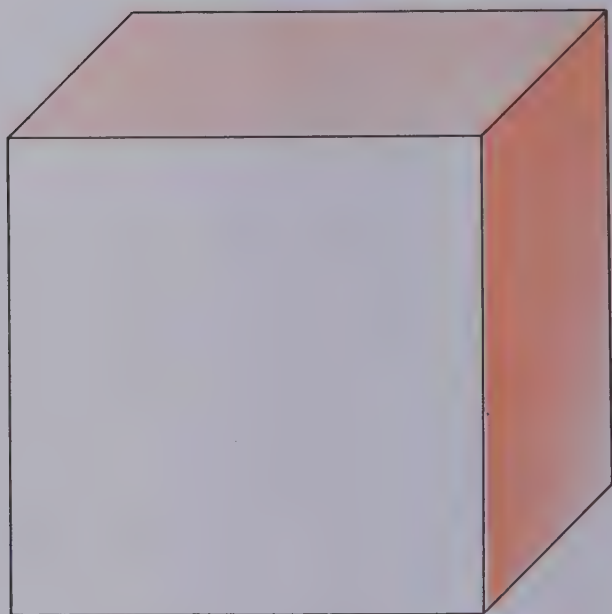
1 cc = 2.7 grams of Aluminum



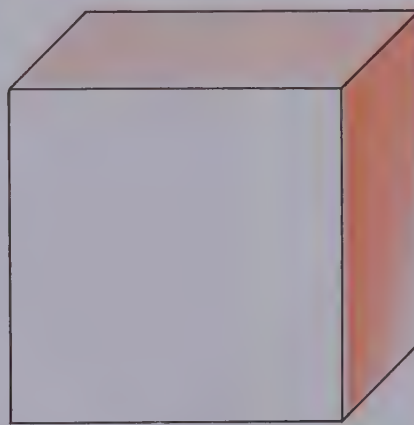
1 cc = 7.8 grams of Iron



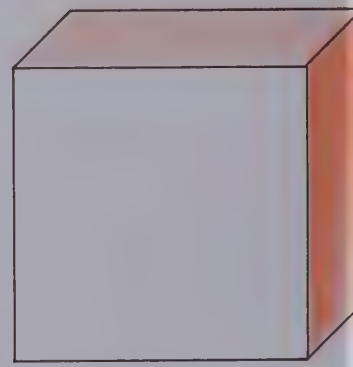
1 cc = 11.3 grams of Lead



500 grams of Aluminum
has a volume of 185.2 cc.



500 grams of Iron
has a volume of 64.1 cc.



500 grams of Lead
has a volume of 44.3 cc.

Each kind of matter has a different density; this makes density an important identifying property of matter since it can be used to help distinguish one kind of matter from another.

Problems:

1. Since 1 cc of copper has a mass of 8.9 g, as we know from its density, what would be the mass of 10 cc of copper?
2. What would be the mass of 5 cc of iron?
3. What volume of iron would have a mass of 39 g?
4. The density of lead is 11.3 g/cc. What volume of lead would have a mass of 56.6 g?

1-12. THE CONCEPT OF EQUILIBRIUM

If you fill a beaker with water to a certain level, mark the level, then place the beaker in a transparent sealed chamber and observe it for a time, you will find that the water level drops at first, then stops. The water appears to evaporate rapidly, lowering the level; then it appears to stop evaporating, so the level stays the same. Why?



Will the water level drop more in one container than in the other?

Some of the water that evaporates returns to the liquid. If the rate of evaporation equals the rate of return, then the level of the water in the beaker will not change. This will happen in the sealed chamber because the evaporated water cannot escape. Such a system is called a closed system. Strictly speaking, equilibrium can exist only in a closed system.

Equilibrium is a dynamic condition, because particles of matter are constantly exchanging places even though we cannot observe them. *Equilibrium is a dynamic state in which two opposing processes are going on at an equal rate, and in which there are no observable changes in the properties of the system.*

1-13 · THE CONCEPT OF MINIMUM ENERGY VERSUS MAXIMUM RANDOMNESS

Another important concept in chemistry is that of two tendencies which cannot be achieved at the same time. You cannot sleep and play football at the same time. It is not possible to sit in class and walk down the hall at the same instant. You do one or the other. Sometimes you may compromise. If you become very tired sitting in class, you may walk to the pencil sharpener or stretch in your seat in order to have some physical activity. These are some models which may help you to understand the opposing tendencies we are about to discuss.

The Tendency toward Minimum Energy

One fact which becomes apparent as we study matter is that *matter tends to achieve a state of lowest possible energy*. In the solid state, particles have lower energy than they do in the liquid or gaseous state. Water molecules in an ice crystal have less energy than when they are moving about in the liquid state. Knowledge of this general tendency toward minimum energy is helpful because it enables us to explain many changes we observe in matter.

However, not all matter will spontaneously form a solid. Therefore, there must be another factor which operates in determining the state of matter. *This opposing tendency is toward random particle arrangement.*

The Tendency toward Maximum Randomness

When we speak of a random arrangement of particles, we mean they are scattered about in a great variety of ways. Randomness implies disorder. If you examine a crystal, you find that it has a definite pattern; the particles which compose it are arranged in an identifiable order. In fact, the order is so definite that we can classify crystals according to the patterns they exhibit.

It becomes apparent, then, that molecules cannot be in a state of lowest energy, as in a crystal, and in a state of great randomness, as in a gas, at the same time. Solids have lower energy and greater order than liquids. Liquids have more energy, and their molecules are more random, than solids at the same temperature. Gases are the most random of the three states of matter, and their molecules have the greatest energy.

Spontaneous Changes

A change will be spontaneous for two reasons, and these reasons are closely related. One reason is related to minimum energy. A change will tend to take place if a lower energy state can be reached. Thus, a stone rolls downhill by itself, but never uphill by itself. The second reason involves randomness.

A change will tend to take place if a more random state can be achieved. Sugar dissolves in water spontaneously. The sugar molecules are more random, more scattered about, in the water than they were in the sugar cube or in the teaspoon.

Often, these two tendencies are in conflict. The molecules of liquid water are more random than they are in solid ice, but they also have more, not less, energy. Ice melts when the temperature is greater than 0°C because, at the warmer temperatures, the tendency to be more random is stronger than the tendency to have minimum energy. Water freezes by itself when the temperature is below 0°C because, at these lower temperatures, the tendency toward a minimum possible energy overcomes the tendency for greater randomness.

A match burns because energy is released and the carbon dioxide and water molecules formed have more randomness than the original molecules of cellulose (in the wood) and molecules of oxygen in the air. Since energy is released when the match burns, the carbon dioxide and water have less energy. When a match burns, both tendencies are achieved, toward less energy and toward more randomness.

When sugar molecules dissolve, energy is absorbed, but the molecules can become more random. At very low temperatures, however, the increase in randomness is not as effective as at higher temperatures. Only a little sugar will dissolve in cold water compared to the amount that will dissolve in hot water.

In general, when food is digested, the molecules formed have more randomness after digestion than before. Food can be digested because the tendency for more randomness is greater than the tendency for lower energy.

Suggestions for Creative Work

1. Determine the percentage of silver in an old dime, using the property of density. The other metal in an old dime is copper.
2. Devise a method for determining the density of table sugar.
3. How might you determine the temperature of the different regions in a burner flame? The temperature of a candle flame?
4. What happens when iron rusts? Devise a controlled experiment to study this reaction.
5. Using marble chips, CaCO_3 , devise a method for determining the mass of one cubic meter of marble, assuming it has the same composition as the chips.
6. What has aluminum to do with the Washington Monument in Washington, D.C?
7. What precious gems contain compounds of aluminum?
8. Why should lye not be placed in aluminum containers?
9. Matter does not always react the same when heated in air. Plan an experiment in which you heat: (a) a 5-cm strip of magnesium ribbon, (b) 2-3 small crystals of copper sulfate, (c) a 1-cm \times 2-cm strip of copper foil. Predict what you think may happen before testing them. Then make the

tests, record your observations, and draw conclusions on the basis of your evidence.

10. Devise an experiment to test the accuracy of a laboratory thermometer.

Suggestions for Creative Writing

A science student must learn to be a good observer. We become so accustomed to our surroundings that often we fail to notice the significance of the "little things" about us. To sharpen your powers of observation and your ability to record or communicate what you observe, the following suggestions are made for creative writing.

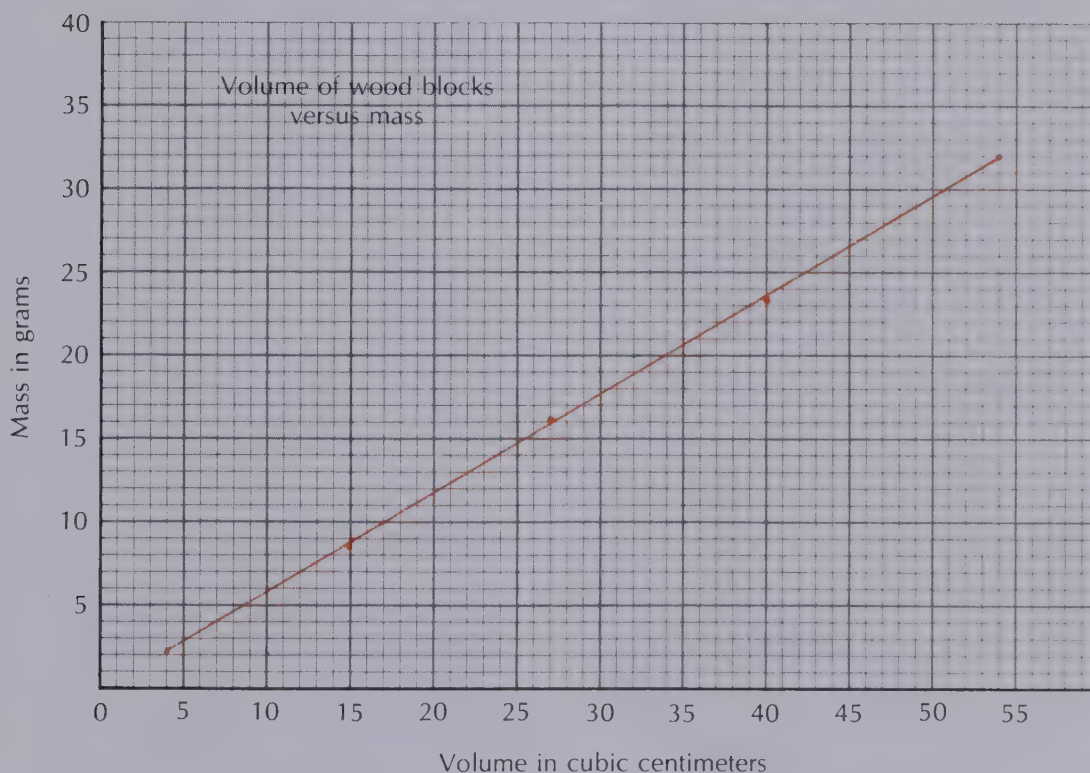
1. Sit in a familiar place for 15 minutes and make a list of *sounds* not really noticed before. Describe these sounds.
2. Walk a familiar route and make a list of the objects not really *seen* before.
3. Sit in a familiar place or walk a familiar route and note the *odors* of which you have not been conscious before. Describe these odors.
4. Eat a selected meal and note the taste of foods which you have been taking for granted. Describe these tastes.
5. Write a poem about something you thought about as you did one of the suggested activities. Select colorful words so that your reader may experience the same sensations you experienced, although he was not there.

Practice Exercises (Answers on p. 307)

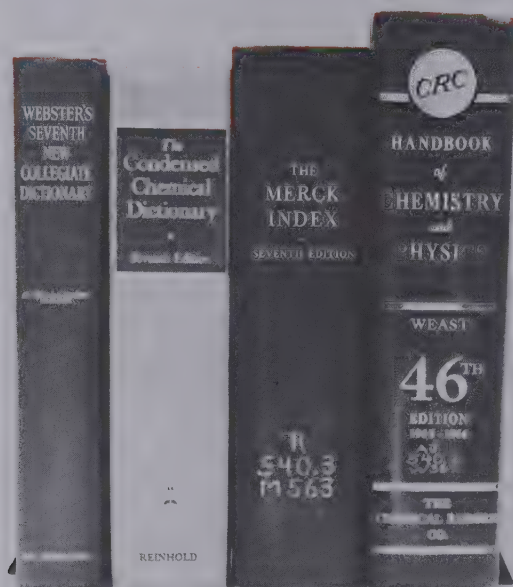
1. Give the metric equivalents for the following:
 - a. 5 cm = ____ mm
 - b. 3 liters = ____ cc
 - c. 60 g = ____ mg
 - d. 25 cc = ____ liter
 - e. 250 cc = ____ liter
2. Determine the number of significant figures in the following:
 - a. 134.80 m
 - b. 1700 g
 - c. 10035.00 cc
 - d. 0.0065 cm
 - e. 250 cc
3. Add the following numbers and give the answer in the proper number of significant figures.

a. 507	b. 15.0607	c. 0.9	d. 6530	e. 0.006
8	3.00	0.0075	45.3	0.100
<u>0.06</u>	<u>0.08</u>	<u>1.31</u>	<u>1.00</u>	<u>0.030</u>
4. Multiply the following numbers and express your answer in the proper number of significant figures.
 - a. 3.4×0.6
 - b. 84.60×0.005
 - c. 109.03×1.50
 - d. 15.7×4
 - e. 2.97×2.5
5. Divide the following numbers and express your answer in the proper number of significant figures.
 - a. $66.3 \div 2$
 - b. $0.942 \div 0.03$
 - c. $124 \div 10$
 - d. $0.0002 \div 0.02$
 - e. $16 \div 4$

6. Solve the following density problems. Show how you arrive at your answers.
- The density of copper is 8.9 g/cc . What is the mass of 5.67 cc of copper? Express your answer in the proper number of significant figures.
 - We know that 250 cc of pure water at 4°C has a mass of 250 g . What is the density of water to the proper number of significant figures?
 - A piece of silver has a volume of 10 cc and a mass of 105.0 g . What is the density of silver? Give your answer to the proper number of significant figures.
 - Sulfur has a density of 2.0 g/cc . If a block of sulfur has a mass of 64.30 g , what is the volume of the block? Give your answer to the proper number of significant figures.
7. A student determined the density of zinc to be 6.8 g/cc . The accepted value is 7.2 g/cc . Calculate the experimental error and the percentage error.
8. Examine the graph below and answer the following questions by reference to the graph.
- What is the independent variable? Give a reason for your answer.
 - What is the dependent variable? Give a reason for your answer.
 - What is the predicted mass at zero volume?
 - Determine the slope of the line. Explain what this slope means in terms of the two variables.
 - Assuming that the blocks are all cut from the same piece of wood, what is the expected volume of a block whose mass is 25 g ?
 - What is the density of the wood? Explain how this is related to the slope of the line.



9. Using a *Handbook of Chemistry and Physics*, locate the following information. Give the publication date of the edition you used and list the page number on which you located the answer to each question.
- The ionic radius of gold.
 - The antidote for mercuric chloride poisoning.
 - The discoverer of platinum.
 - The major properties of Freon-21, a common refrigerant.
 - The shape of potassium permanganate crystals.
-



-
10. List the properties by which we may recognize an equilibrium system.
11. Using the concepts of minimum energy and maximum randomness, explain:
- Why ice melts spontaneously at room temperature.
 - Why sugar dissolves in water.
12. (Multiple Completion; see special directions in Appendix 13)
- Solids are characterized by
- indefinite volume
 - indefinite shape
 - ability to diffuse rapidly
 - relative incompressibility

Self-Test (Answers on pp. 307 to 309)

- The following will be in the form of practical tests; you will be expected to show that you can do each one.
 - Identify the uses and give the names, properly spelled, of all laboratory apparatus you are using.

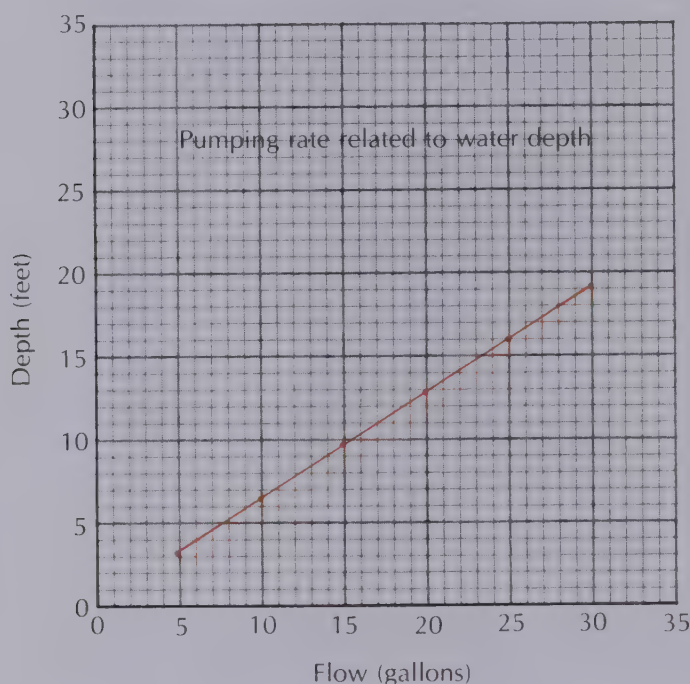
- b. Demonstrate the laboratory techniques described in the laboratory manual.
- c. Use the laboratory balance to determine the mass of objects.
- d. Determine the volume of liquids, using graduated cylinders.
- e. Determine the density of a solid (maximum error: 5%).
2. Review safety rules and the reasons for observing each.
3. A student calculated the density of tin to be 7.0 g/cc. The accepted value is 7.3 g/cc. Calculate the percentage error.
4. Using the formula for density, solve the following problems. (Use significant figures.)
 - a. The density of mercury is 13.6 g/cc. What is the mass of 9.30 cc of mercury?
 - b. If a piece of nickel has a mass of 45.1 g and a volume of 5.06 cc, what is the density of nickel?
 - c. The density of magnesium is 1.74 g/cc. What is the volume of 6.70 g of this metal?
5. Give the following metric equivalents:
 - a. 10 cm = ___ m
 - d. 10 cg = ___ g
 - b. 1500 ml = ___ liters
 - e. 1 cm = ___ m
 - c. 0.5 kg = ___ mg
 - f. 25 cc = ___ liter
6. Determine the number of significant figures in each of the following:
 - a. 0.089 kg
 - d. 10.000 cc
 - b. 37.020 g
 - e. 670 g
 - c. 400,600 m
 - f. 15 kg
7. A student heated water to the boiling temperature. He then turned off the fire, and recorded the water temperature every 2 minutes for about 20 minutes. His data are given below. Graph the ordered pairs, and answer the questions concerning the data.

DATA TABLE

Time, min	Temperature, °C
0	96.2
2	88.6
4	82.3
6	76.0
8	73.8
10	68.3
12	65.0
14	60.5
16	58.1
18	54.4
20	50.2
22	46.1

- a. What is the independent variable? Give a reason for your answer.
- b. Is the relationship between the two variables linear or nonlinear?
- c. Determine the slope of the line.

- d. What is the predicted temperature at 26 minutes?
 - e. Why would the temperature probably never drop to 15°C , even if the student observed it for several hours?
 - f. Suppose the line for another set of ordered pairs also slanted downward to the right, but the slope was $2.0^{\circ}\text{C}/\text{min}$. How much would the temperature decrease in five minutes?
 - g. Suppose that in still another experiment a student found that the temperature decreased 3.5°C each minute. After he makes his graph, what will the slope be?
8. Water was pumped into a storage tank, and the depth of water was measured at intervals. The data are plotted below. Examine the graph and answer the following questions.

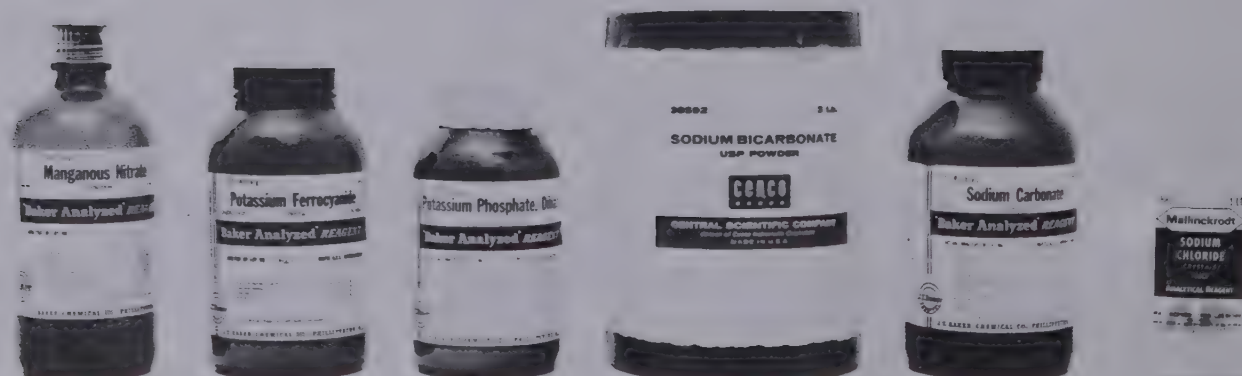
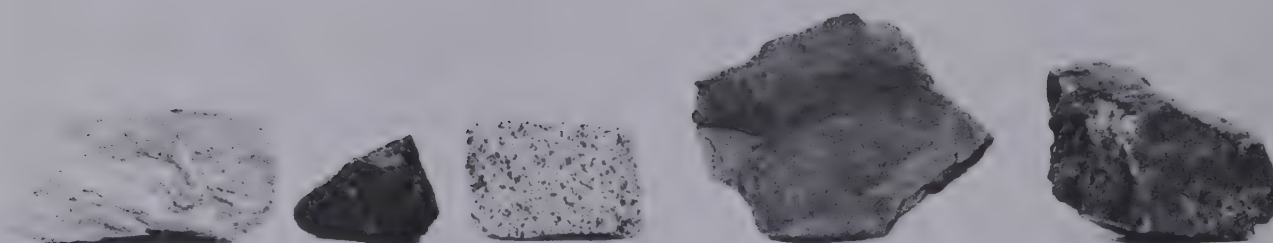
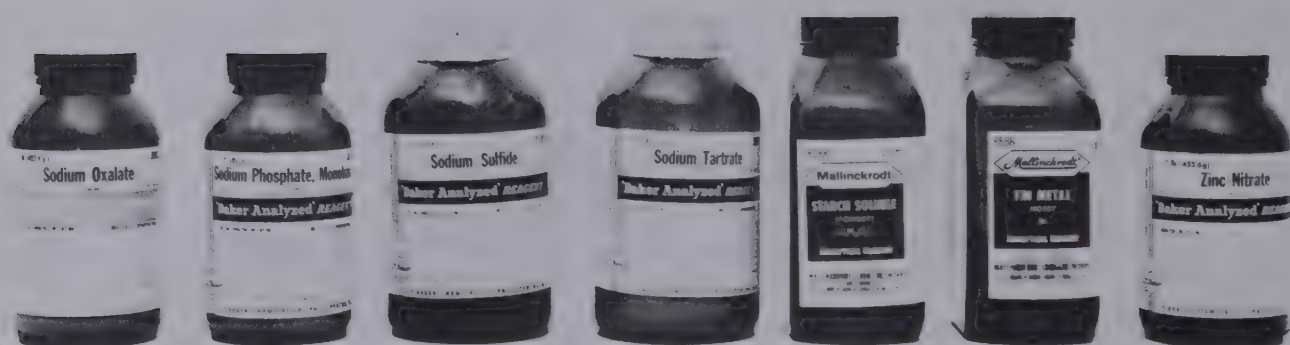
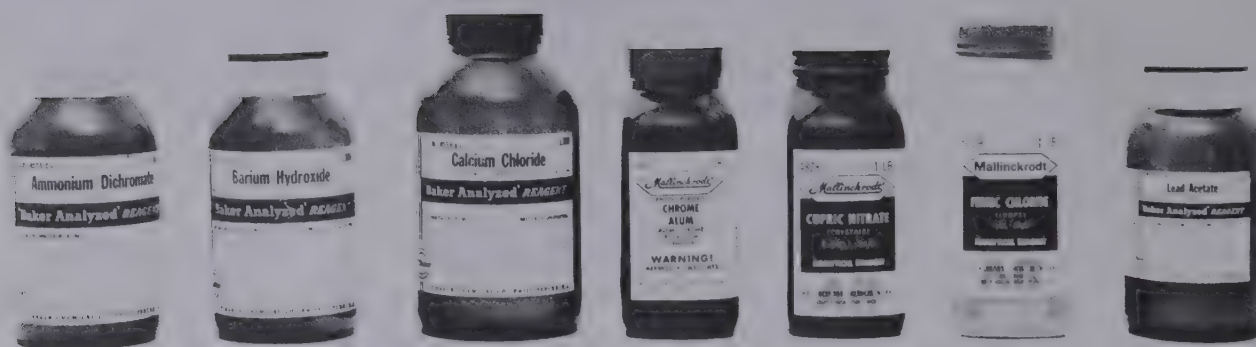


- a. What is the independent variable? Give a reason for your answer.
 - b. Determine the slope of the line.
 - c. What is the mathematical equation for the relationship described?
 - d. What is the expected depth of water when 35 gallons have been pumped into the tank?
9. Locate the following information in the *Handbook of Chemistry and Physics*. Be sure to give the date of publication of the edition you use and list the page number on which you find each answer.
- a. What is the density of yttrium carbide?
 - b. Who discovered lithium?
 - c. How do we convert scruples to pennyweights?
 - d. What is the crystal symmetry of cobalt chloride, CoCl_2 ?
 - e. How do we prepare the laboratory reagent antimony pentachloride?

10. Talk with your teacher or the school librarian about scientific journals. Examine a copy of each available periodical, then list three current periodicals which a chemistry student might like to read regularly as a part of his study.
11. (Multiple Completion; see special directions in Appendix 13)
Precision in measurement implies
 1. closeness of a measurement to an accepted standard
 2. no uncertainty
 3. that the measurement is exact
 4. agreement between two or more sets of measurements taken with the same instrument

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For the student who wants to know more about atomic weight determination.





CLASSIFICATION OF MATTER

OBJECTIVES:

By the time you have completed your study of Chapter 2, you will be expected to demonstrate acceptable performance on the following objectives.

1. Given a list of properties of matter, *classify* each as either (a) physical or (b) chemical.
2. Given a list of changes in matter, *classify* each as either (a) physical or (b) chemical.
3. Given samples of matter, *recognize* which are homogeneous and which are heterogeneous.
4. Given samples of elements, *recognize* which are metals and which are nonmetals.
5. Given a mixture, *determine* a method for separating it into its components.
6. Given a sample of matter and instructions for changing it, *determine* whether the observed change is physical or chemical.
7. Given several samples of matter, *devise* a convenient system for classifying them.
8. *List* the distinguishing properties of the three states of matter: solids, liquids, and gases. *Explain* how these properties apply to each of the three states.
9. *Describe* changes in state, using the concepts of minimum energy and maximum randomness.
10. *State* the definitions for: element, compound, metal, nonmetal, and metalloid.
11. Given a graph of the heating-cooling curve for a substance, *determine*:
 - a. Whether the substance is pure or a mixture
 - b. If pure, the melting temperature and the freezing temperature.
12. *State* the percentage distribution by weight of the three most abundant elements in the lithosphere and atmosphere.
13. *Describe* the formation of a compound, using the Law of Definite Composition.
14. *State* the major differences between compounds and mixtures.
15. *Explain* how potential energy changes with distance (a) when like charges are involved and (b) when unlike charges are involved.
16. Given a compound, *devise* a method for separating it into simpler substances.
17. *Recognize* the symbols for the common elements, including some which are not derived from their English names.
18. Given the names of common elements, *write* their symbols.

SUGGESTED ORDER OF STUDY

Note: You are expected to do outside reading, free labs, and other creative work at appropriate times. These activities should be placed in this suggested schedule as you see fit.

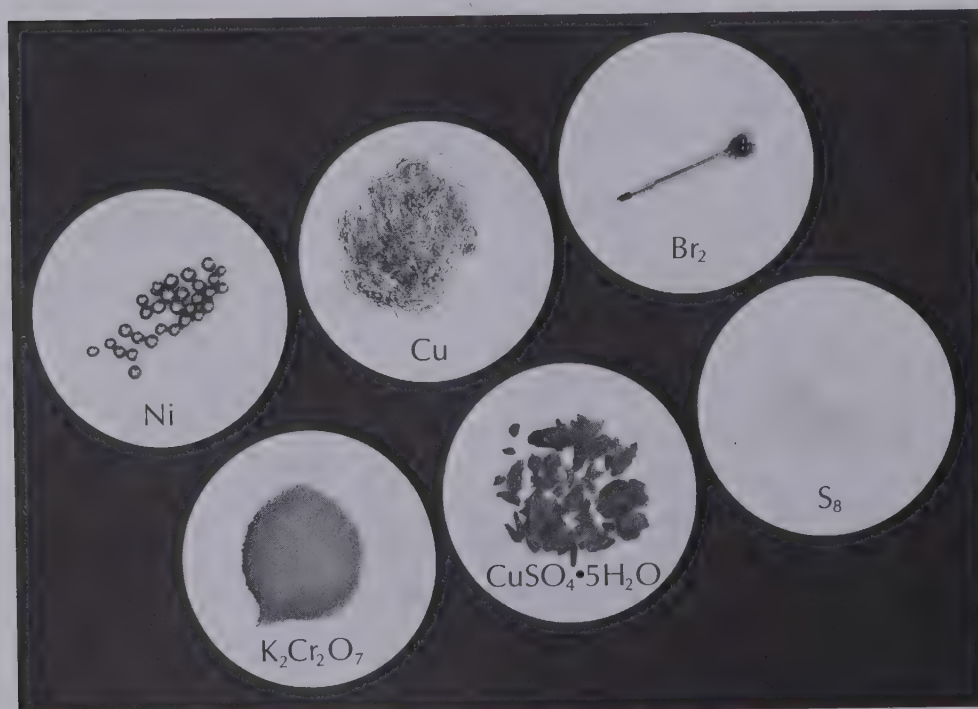
1. Perform Exp. 2-1 and hand in formal report.~
2. Study Sec. 2-1 in the textbook.
3. Perform Exp. 2-2 and hand in formal report.✓
4. Perform Exp. 2-3 and hand in formal report.✓

5. Study Sec. 2-2.
6. Perform Exp. 2-4 and hand in formal report. ✓
7. Study Secs. 2-3 through 2-5.
8. Perform Exp. 2-5 and hand in formal report. ✓
9. Study Secs. 2-6 through 2-8.
10. Learn the symbols for the elements assigned by your instructor.
11. Take the Self-Test. Review portions of chapter as needed.
12. Take the test for Chapter 2. This test will include a laboratory practical in which you will be asked to identify different types of matter as stated in the chapter objectives.

2-1 • PROPERTIES AND CHANGES IN MATTER

As you attempted to classify the samples of matter in Exp. 2-1, you found that it was relatively easy to distinguish homogeneous matter from heterogeneous matter. However, to determine whether matter is an element or a compound requires more information than one can obtain by inspection. What criteria did you use for sorting the solids into metals and nonmetals? Perhaps you knew from experience that most metals are shiny and that nonmetals are not. The characteristics by which we recognize matter are known as *properties*. Before we can make much progress in our study of the classification of matter, we must become familiar with those characteristics known as physical properties and chemical properties, and the chemical changes that occur as we investigate matter.

Those properties of matter which can be investigated without changing the composition of a substance are known as *physical properties*. These include color, odor, density, and melting point. Often, physical properties can be



An assortment of pure, laboratory chemicals.

used to identify a substance. For example, a certain liquid substance has no color and no odor; its density is approximately 1 g/cc. This substance boils at 100° C, normally, and freezes at 0° C. By knowing its physical properties, you can identify this substance as water.

There are many other physical properties, of course. Hardness is one. If you knew that some unknown substance was either a diamond or a piece of cheese and you were told that the substance was very hard, it must then either be a diamond or a very, very stale piece of cheese.

Crystalline form is another physical property. Take note of the illustration of crystals of several different substances, each with a different appearance. Notice that this physical property also helps us to identify substances.

An assortment of natural crystals.



Chemical properties can be investigated by causing changes in the composition of matter. Chemical properties describe how a substance reacts, or changes, to form new kinds of matter. Think of the physical properties of a piece of wood, such as a toothpick. Then think of the physical properties of a charred toothpick, after it has burned for awhile. The physical properties have changed; the composition has changed. A new kind of matter is present. The ability to change, by burning, is a chemical property.

There are many other examples of chemical properties. When a plant grows, the physical properties of the fertilizers change; some of the components of the soil change; and the air that the plant used in growing changes;

new kinds of matter are formed. The presence of the new kinds of matter indicates that the growth of a living plant is a chemical change.

It is a chemical property of a bottle of soda, or soft drink, to change by releasing bubbles of gas when the bottle is opened, or when sand is sprinkled into the liquid. Did you ever notice the difference in taste of a soft drink after some practical joker has sprinkled sand into your bottle of soda? The physical property of taste has changed; the kind of matter present is different.

Odor, taste, hardness, crystalline form, color, density—all of these and others are physical properties. If any of them has changed, we can expect to find a different kind of matter.

So, when physical properties change and different kinds of matter appear, the change is said to be a chemical change. When physical properties do not change and no new matter is formed, the change is called a physical change. For example, suppose you bend a toothpick or compress a spring. These would be examples of physical change. The kind of matter in the toothpick and the spring stays the same although you have changed the condition of the matter in both.

When you burn the toothpick, the physical properties are changed; new matter appears; the burning of a toothpick is a chemical change.

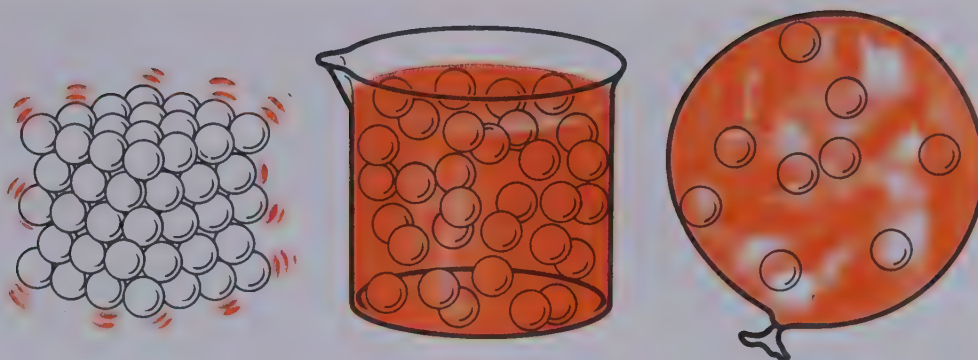
Suppose you melted a piece of ice. Is this a chemical change or a physical change? To answer this kind of question, we always ask: Did new matter form? The physical properties of water are different from the physical properties of ice, but the composition of ice and water is the same. So, no new matter is formed when ice melts; therefore, the change is a physical change.

Most scientists say that for a change to be a chemical change, the composition must change. Some modern scientists, however, define a chemical change as a change of physical properties, even when the composition does not change. Using this definition, they would say that the melting of ice is a chemical change. Difficulties such as this do not happen too often. Usually, it is quite clear that both the physical properties and the composition change. All such changes are chemical changes.

When a piece of paper is burned, light and heat are given off, and the ash that remains has properties and composition quite different from those of the paper. When we pass a current of electricity through water to which a small amount of acid has been added, we obtain oxygen gas and hydrogen gas. These gases do not resemble water in any way. Thus, we see that when a chemical change occurs, the new substances produced by this change have properties very different from those of the original material. The action of hydrochloric acid and sodium hydroxide on aluminum foil, which you will observe in Exp. 2-2, illustrates chemical change.

2-2· CHANGES IN THE STATES OF MATTER

As you know from experience, it is easy to classify matter according to whether it is a solid, a liquid, or a gas. We can summarize the differences among these states of matter by comparing four of their general physical properties (Table 2-1).



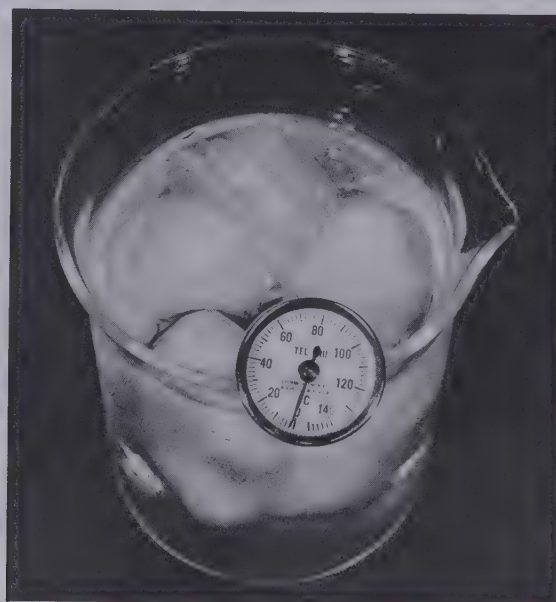
Characteristics of the States of Matter

State	Shape	Volume	Compressibility	Ability to Diffuse
solid	definite	definite	practically none	usually slight
liquid	varies	definite	very slight	diffuses slowly
gas	varies	not definite	great	diffuses rapidly

Table 2-1

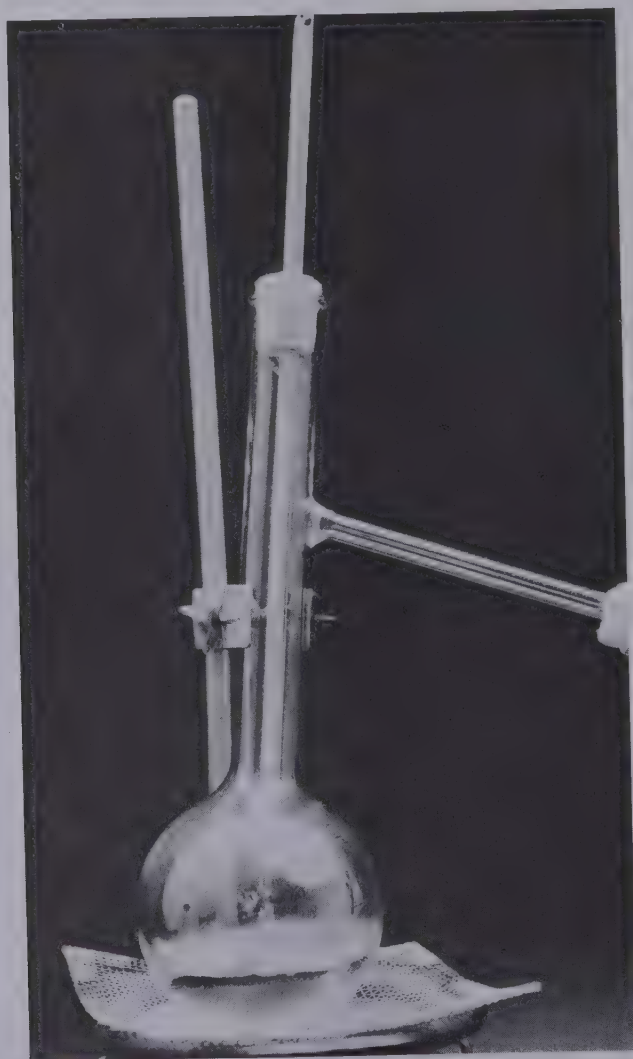
You have observed water freezing, ice melting, and water evaporating. Why does matter change from one physical state to another? How can we explain the change of state? Does a time-temperature graph of a melting solid reveal any information about the composition of the solid? In order to answer these questions, let us consider the melting of ice. When ice is kept at temperatures below 0°C , the normal melting point of ice, the molecules in the crystal vibrate in fixed positions. As the temperature is slowly raised, the vibratory motion of the molecules increases. Finally, when the ice has warmed up enough to reach the melting point at 0°C , the molecules have sufficient energy to move out of the crystal pattern. This change of state is called *melting* or *fusion*.

How will the amount of ice in the beaker change if the water temperature is higher than 0°C ?



In Exp. 2-3 you found that during the melting of a pure substance the temperature of the system did *not* change even though heat was supplied continuously. When a time-temperature graph was plotted for the heating and melting of a pure substance, you found a plateau. The temperature represented by such a plateau is the melting temperature of that particular substance. Once melting is complete, the temperature of the liquid then rises as heat is added. What happens to the heat that is supplied during the melting process? Why does it not cause the temperature of the system to rise? Propose a hypothesis to explain these observations. Could the same kind of experiment be done with water?

As we continue to heat water after all the ice has melted, the energy of the molecules increases. More and more of the molecules have enough energy to escape from the liquid as gaseous particles. When the temperature reaches 100°C , it stops rising and the water boils. Again we find, if we plot a time-temperature graph, that during boiling there is no change in the *temperature* of the system even though we are still adding heat. Why?



What is happening to the energy in this system as the liquid boils?



Solid mercury, frozen by surrounding it with a mixture of Dry Ice and acetone.



The solid mercury is placed in a dish.



The mercury absorbs heat from the air and begins to melt.



As more heat is absorbed, the mercury becomes totally liquid.

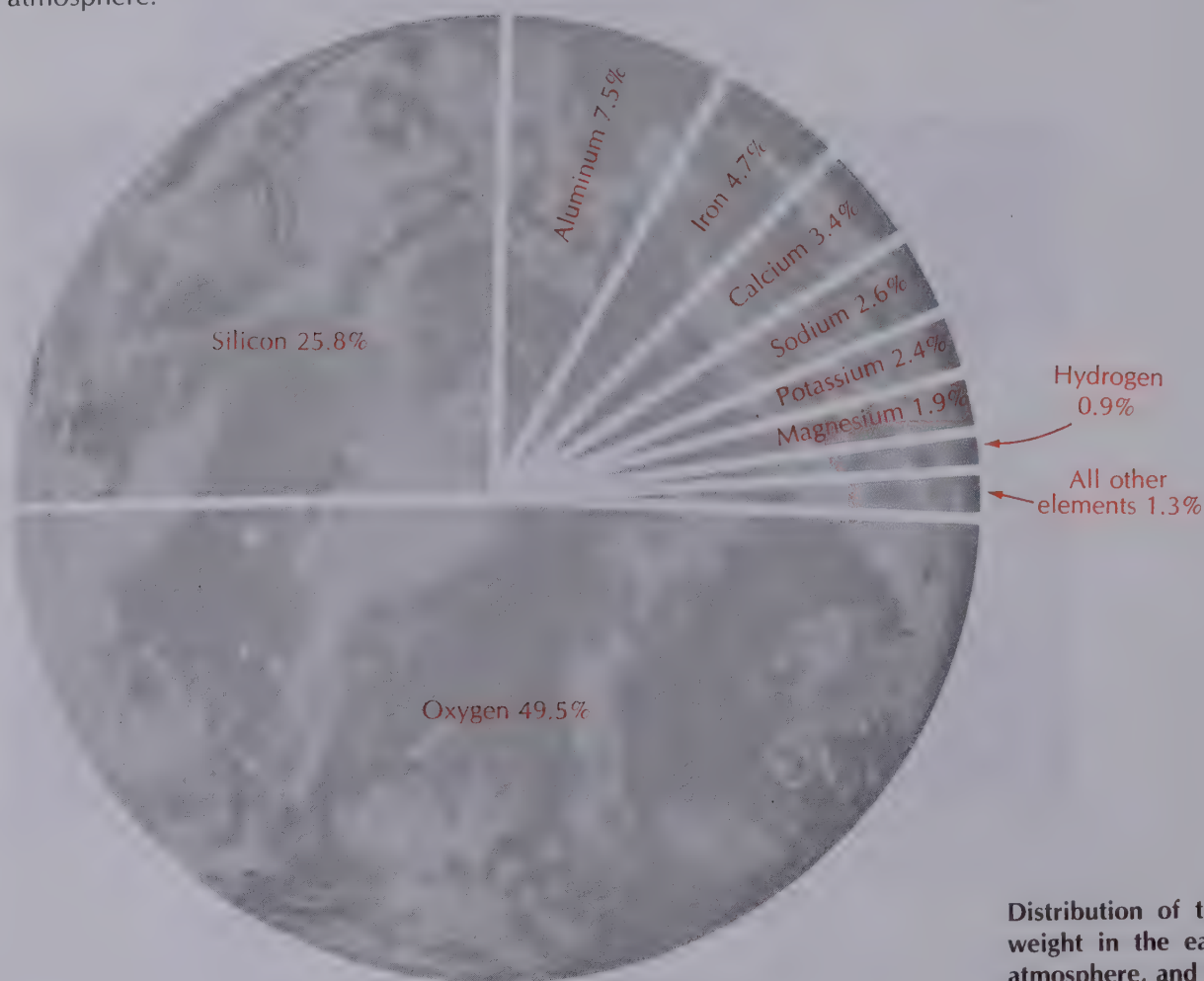
2-3 • ELEMENTS

In the classification of matter we find it convenient to group homogeneous (pure) substances into two classes: elements and compounds. An element is defined as a substance which cannot be separated into different kinds of matter. An element is the simplest form of matter. For this reason elements are often called the building blocks of the universe. There are 89 elements which occur naturally. More than 100 elements are known today. Many of these are man-made, and research scientists are still adding elements to the list. No one knows yet how many man may be able to produce in the laboratory.

About one-third of the natural elements are well known. A few, such as gold, silver, and sulfur, have been known since the dawn of recorded history.

Elements in the Earth's Lithosphere and Atmosphere

The skin of the earth is a few miles thick. This does not seem thin to us; however, it is thin when we compare it to the earth's diameter. In fact, by comparison, it is thinner than an egg shell. The earth's skin is called the *lithosphere*; it includes the rocks, soil, mountains, and oceans. More than three-fourths of the earth's skin is composed of only two elements: oxygen and silicon. The graph gives the percentages for the other elements in the lithosphere and atmosphere.



Distribution of the elements by weight in the earth's crust, the atmosphere, and bodies of water.



The Bumpass Hell area of Mount Lassen Volcanic National Park. What chemicals are associated with this region?

Metals and Nonmetals

Elements can be classified further as metals and nonmetals on the basis of their properties. In general, *metals* are solids which have a luster and are good conductors of heat and electricity. Aluminum and copper are examples. Many metals can be hammered or pressed into thin sheets, as lead, tin, and aluminum. Others can be drawn into a wire, as copper and platinum. Not all metals possess these properties to the same degree. There is one metallic element which is a liquid at room temperature. Do you know its name?

Generally speaking, *nonmetals* are not shiny, are not good conductors of heat and electricity, and cannot be hammered into sheets or drawn into wire. Oxygen, sulfur, and carbon are examples of nonmetals. There is one nonmetal element that is a liquid at room temperature. What is it?



Sulfur (left), a nonmetal, and pieces of silicon, a metalloid, on a sheet of aluminum, a metal.

In most systems of classification we find borderline cases. This is true in the grouping of elements into metals and nonmetals. A few elements have properties similar to both metals and nonmetals and are known as *metalloids*. Silicon, arsenic, and antimony are examples. Silicon is usually classified as a nonmetal, but may react like a metal in certain chemical changes. Arsenic and antimony are often grouped with the metals, but may react like nonmetals under certain conditions.

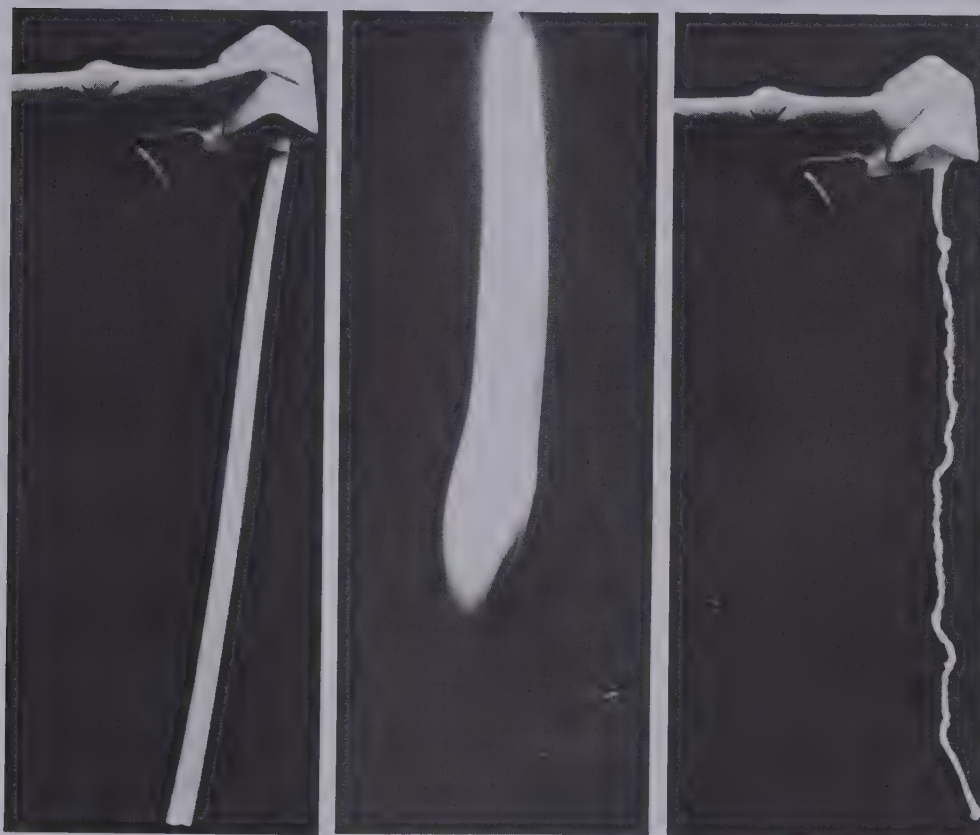
2-4. COMPOUNDS

Elements combine chemically to form compounds. All known compounds are composed of two or more elements. Common table salt, for example, is composed of the two elements sodium and chlorine; water is composed of the two elements hydrogen and oxygen. Baking soda is composed of four elements:

sodium, hydrogen, carbon, and oxygen. All of these, salt, water, and baking soda, are compounds.

A compound is defined as a homogeneous substance composed of two or more elements chemically combined in a definite proportion by weight. When a compound is formed, the elements lose their identifying characteristics, and the compound has properties different from those of the elements which make it up. For example, water is composed of hydrogen gas and oxygen gas combined in a weight ratio of 1:8. The properties of water are different from those of either gas. Another example which emphasizes the change in properties which occurs when elements unite is that of salt, sodium chloride. Sodium is a silvery, poisonous metal; chlorine is a greenish, poisonous gas; sodium chloride is a white, crystalline solid which is necessary for life.

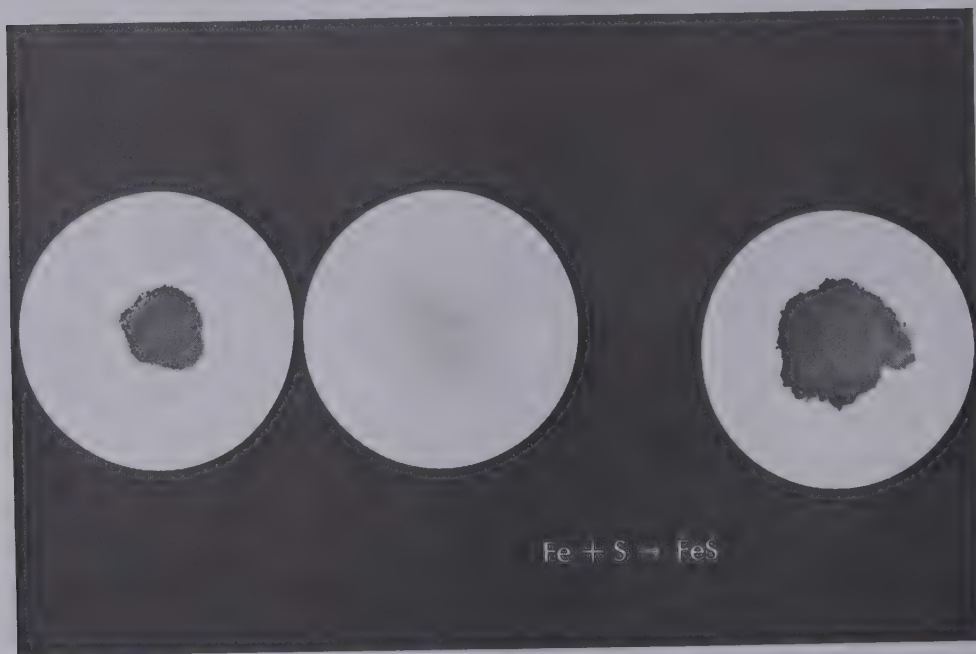
Compounds are formed by chemical action in which energy plays a very important role. In Exp. 2-4 noticeable light and heat were released as the iron and sulfur combined to form iron sulfide. When aluminum foil reacts with hydrochloric acid, a gas is evolved and the test tube becomes warm, indicating that heat is released during the chemical reaction. Production of energy in the form of light or heat or both is usually evidence of chemical change. Although some changes of state release heat, the amount is usually much less than in chemical changes. Chemical changes which *release* heat are known as *exothermic* reactions. What reactions that *absorb* heat (*endothermic* reactions) can you think of?



(Left) A piece of unburned magnesium ribbon. (Center) The ribbon as it burns. (Right) The magnesium oxide ash that is produced.

The Law of Definite Composition

You were told to use 7 grams of iron and 4 grams of sulfur in making iron sulfide. Would it be possible to make this compound using other amounts of the elements? Perhaps you experimented with this idea after completing the first reaction. If so, you probably found that when other proportions of iron and sulfur are used, some of one of the elements remained uncombined after the action was complete.

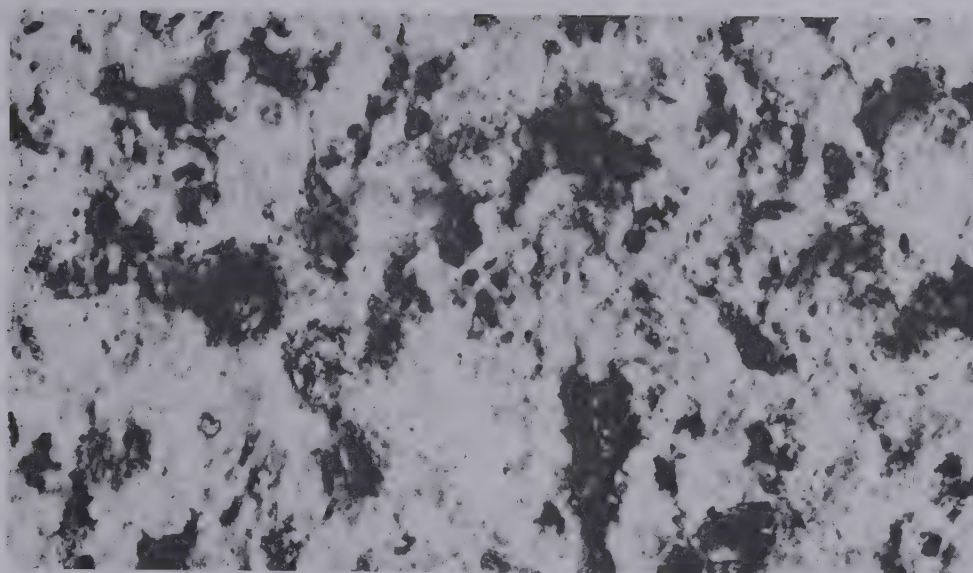


Iron (left) and sulfur (center) can react to produce iron sulfide (right).

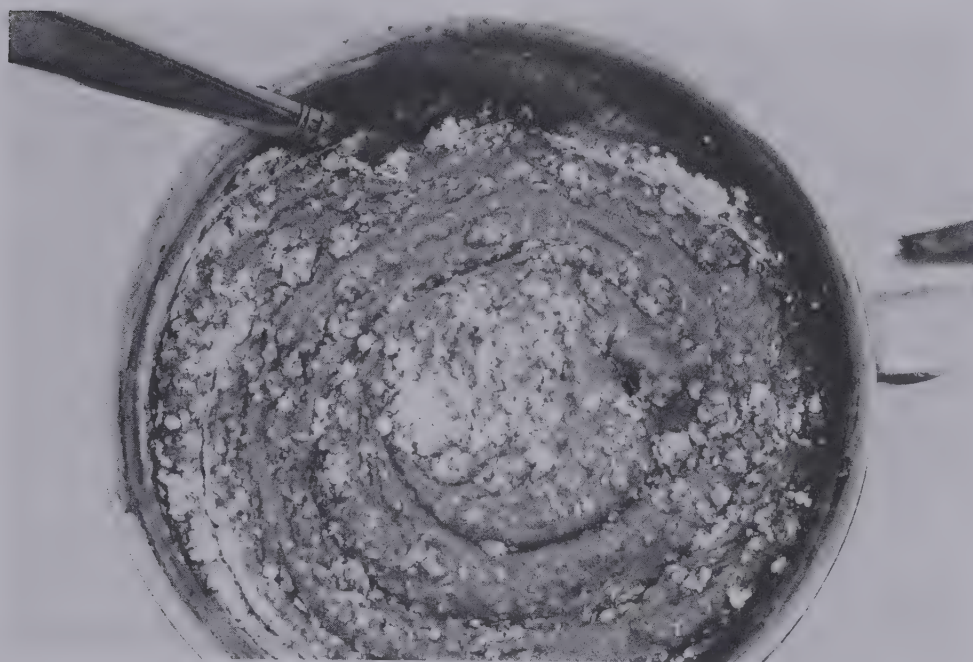
Louis Proust (1755–1826), a French chemist, is credited with being one of the first to report that elements always combine in a definite ratio by weight. This seems reasonable, for if a compound can be recognized by certain properties, it must always be formed by the same elements in the same proportion. The findings of Proust have been confirmed many times and his observation is now known as the *Law of Definite Proportions*: Every compound has a definite composition by weight due to the fixed proportions of the elements of which it is made. (Actually, today we know that there are some exceptions to this law.)

2-5 • MIXTURES

Mixtures are composed of two or more substances not chemically combined. The components of a mixture retain their individual properties and, unlike the elements in compounds, may be present in any weight ratio. Frequently, mixtures are heterogeneous; they have different parts, which may be seen by inspection, as in granite. However, one important class of mixture is homogeneous. This is the class of matter known as solutions.



This closeup view of the surface of a piece of granite shows it to be a heterogeneous mixture of at least two substances.



The partially mixed cake batter in this pan is another example of a heterogeneous mixture. To bake properly, the ingredients in the batter need to be homogeneously mixed.

Ordinary solutions consist of a solid dissolved in a liquid, although there are many other kinds of solutions. A solution is homogeneous because the substance which is dissolved is scattered about in the liquid in such tiny particles that it cannot be observed even with a powerful microscope. So, as far as we can tell, every part of the solution has properties like every other part and is therefore said to be homogeneous. The solution is a mixture because the amounts present can be changed, and they do not unite chemically. Since they are not chemically joined, usually they can be easily separated. Sugar in water is an example of a solution.

To summarize: Elements are the simplest form of matter and are the building blocks for compounds and mixtures. Mixtures and compounds are unlike in these ways:

Mixtures	Compounds
1. Components do not lose identity.	1. Components lose identity.
2. Components can be separated by a simple process.	2. Components can be separated only by chemical action.
3. Components can be present in any proportion.	3. Components are present in a <i>definite</i> proportion by weight.
4. No evidence of chemical action during preparation.	4. Evidence of chemical action in the form of light, heat, gas, or precipitate usually observed during preparation.

Here again there are borderline cases. Some compounds have a variable composition. For example, the "bronzing" paints you may have used to decorate a picture frame, or a "golden vase" for a school play, are tiny flakes of a compound containing the elements sodium, molybdenum, tungsten, and oxygen. Different colors of bronzing paints are all made of the same compound, but with different relative amounts of the four elements.

Also, when some mixtures are prepared, the process is exothermic; heat is evolved. You may have seen, or used, a "chemical hot water bottle." In this device, you prepare a mixture of sodium sulfate and water; it is a true mixture because it meets the first three requirements listed above. But when this mixture is prepared, heat is evolved, as though a compound were being formed.

2-6. ENERGY AND CHEMICAL CHANGE

The change which matter undergoes when compounds are formed is always accompanied by energy changes. In fact, energy is the key which unlocks our understanding of chemical changes.

Energy is associated with work and is frequently defined as the ability to do work. What is work? To the scientist, *work is done when a force acts through a distance*. For example, if you attach a cord to a steel ball and lift it to a height of four feet, you have done work on the ball by lifting it against the force of gravity:

$$\text{Work} = \text{force} \times \text{distance}$$

If a steel ball is lifted to shoulder height, you have done work on the ball. The quantity of energy is equal to the work done. There are two fundamental types of energy associated with matter: kinetic energy and potential energy.

Kinetic Energy

Kinetic energy is defined as energy of motion. Scientists have shown that the kinetic energy of a body depends upon two factors: (1) the mass of the body and (2) the speed of the body—that is, how fast it is traveling. The kinetic energy of an object may be expressed by this relationship:

$$KE = \frac{1}{2} mv^2$$

where m is the mass and v is the speed.



What changes in kinetic energy and potential energy are the skiers undergoing?

The kinetic energy of atoms and molecules is directly proportional to their temperature. As you observed in Exp. 1-4, the potassium permanganate was distributed more rapidly in hot water than in water at room temperature. At higher temperatures the particles have more kinetic energy. Since the masses of the individual particles of water and potassium permanganate remained constant, we can assume that their average speeds increased as the temperature rose.

Particles of matter at the same temperature have the same average kinetic energy. This is a generalization that can be very useful to you as you pursue your study of chemistry.

Potential Energy

Potential energy is usually defined as energy of position. The steel ball we mentioned earlier possessed potential energy after having been raised to shoulder height. This is because the work done on the ball to raise it to that height was stored as energy of position, or potential energy. No one would be likely to put his foot under that steel ball if he thought that you might let go of it. He would know that the raised steel ball has the power to smash toes because of its potential energy due to its raised position. Since you put energy into the ball when you raised it, if the ball were suddenly released, it would do work on someone's toes, or on the floor. When the ball is released, the energy stored in the ball as potential energy is changed into kinetic energy as the ball falls back to the floor. After expending its kinetic energy in falling to the floor, what potential energy does the ball possess?



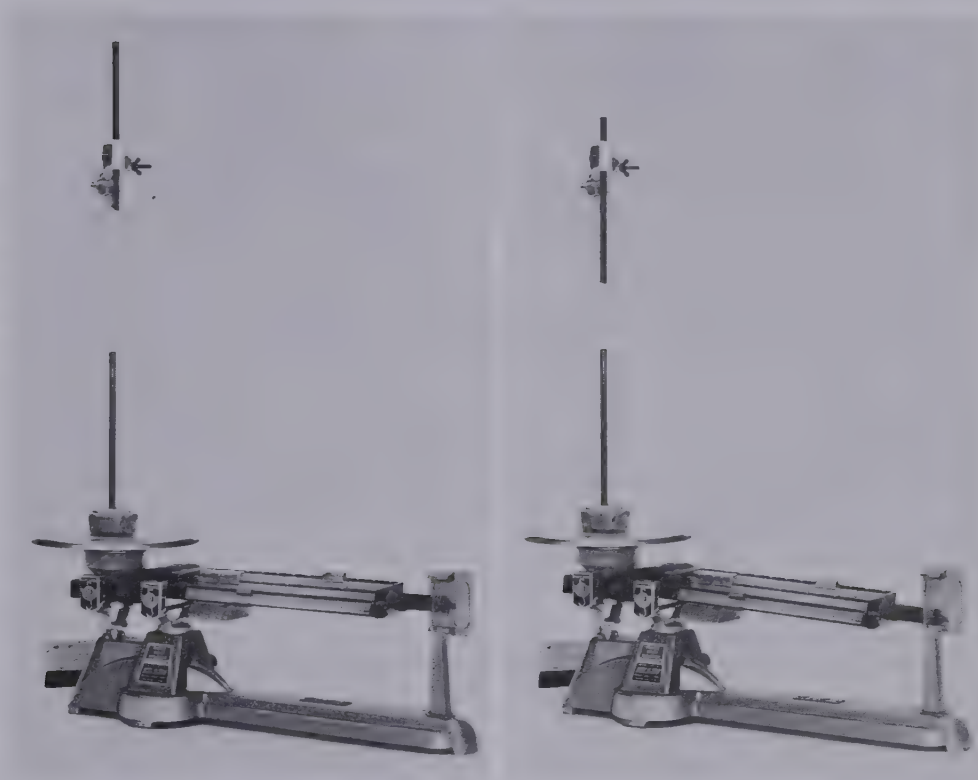
The crane in the picture is lifting a one-ton cement bucket to the various levels of the 35-story building on which the crane is mounted. Consider the changes in both kinetic and potential energy as the bucket is lifted.

Energy is never lost. It may be transformed from one kind to another; some potential energy or kinetic energy may be converted to heat energy by friction, or into electrical energy or other forms of energy. But the total amount of energy is never lost.

We will give much attention to chemical energy. This is a particular kind of potential energy which may be transformed into many other kinds of energy. For example, the food you eat contains stored (potential) energy which is released as heat energy when the food undergoes chemical changes inside your body. Flashlight batteries contain stored chemical energy which is released as light and heat energy when the batteries are used. Describe the energy conversion in a battery-powered transistor radio.

Later, as we study chemical reactions in greater depth, we will be interested in the transformation of kinetic energy to potential energy, and vice versa. For the present let us consider the idea of potential energy changes, using magnets. Magnets are useful in introducing the concept of potential energy and distance, because we can feel and measure the force of attraction between like and unlike magnetic poles.

(Left) The magnets are far enough apart so that the balance does not respond. (Right) The balance responds when the magnets are moved closer together. Are like or unlike poles of the magnet involved?



As you found in Exp. 2-5, when two *unlike* magnetic poles are brought closer together, the force of attraction increases until the magnets come together spontaneously. The nearer their approach, the greater the force acting to bring them together. For *unlike* magnetic poles, decreasing the distance between them results in a *decrease* in potential energy. What will happen to the potential energy of the system as you do work (use kinetic energy) to increase the distance between the unlike poles?

Conversely, when *like* magnetic poles are close together the force of repulsion is greater. As the force of repulsion increases, more and more work must be done to push the poles together. The more work done, the greater the amount of stored (potential) energy. For *like* magnetic poles, decreasing the distance between them results in an *increase* in potential energy.

The potential energy of atoms and molecules in matter may be due to their position, their composition, and their electric charge. The chemist is particularly concerned with the potential energy changes of particles that possess an electric charge. We will return to this concept of energy many times as we study the formation of chemical bonds between atoms in a later chapter.

2-7 · FACTORS INFLUENCING CHANGES IN MATTER

You have observed changes of state as sugar dissolved in water and as paradichlorobenzene melted. The energy changes associated with these changes indicate that the potential energy of the particles in the solid state is lower than that in the liquid state. In the solid state the particles attract each other with considerable force, as indicated by the fact that the solid does not change shape. When the force of attraction is great, potential energy is low. When heat is applied, it increases the kinetic energy of the particles to a point where the force of attraction between them is overcome and the solid dissolves or melts. Since work is done in overcoming the attractive forces in the solid, the potential energy of the liquid state is greater than that of the solid state.

The tendency to seek a state of minimum energy is one of the factors that influences change. How is it, then, that all substances do not spontaneously form solids if this represents the state of minimum energy?

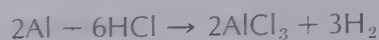
We must remember that there is an opposing tendency also influencing change. This is the tendency toward maximum randomness. The liquid state is more random than the solid state because there are many more ways in which the particles can be arranged. When these two tendencies oppose each other, the dominant one prevails. Heat influences molecular motion, and in the experiment where it was applied to the paradichlorobenzene crystals, heat was the determining factor in causing randomness to prevail over minimum energy. Increased molecular motion favors disorder. It is not easy to predict which tendency will be favored in any given reaction. This must be determined by experimentation.

2-8 · CHEMICAL SYMBOLS

Chemists have developed a shorthand system for representing the elements. Not only is this more convenient than writing out the name of the element, but when symbols are used to summarize a chemical reaction, it is much more clear and concise than writing the same thing in words. For example, if you were to write in words the reaction between aluminum and hydrochloric acid, you might say:

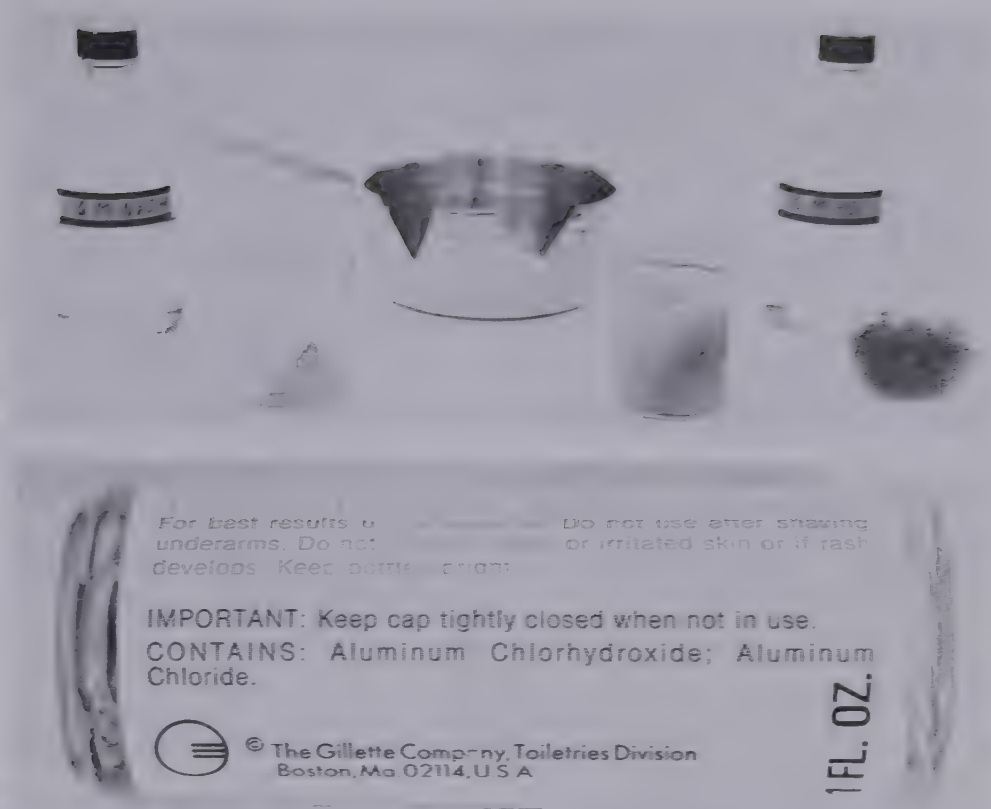
"Two moles of aluminum atoms reacted with 6 moles of hydrogen chloride molecules to produce 2 moles of aluminum chloride molecules and 3 moles of hydrogen molecules."

Now compare this with the chemical shorthand method of expressing the same thing:



As in all shorthand systems, we have to learn to read the symbols.

Until the nineteenth century, drawings and other awkward methods were used to represent the elements. Jons Jakob Berzelius (1779–1848), a Swedish chemist, devised the symbol system in use today. His method consists of using the first letter in the name of the element as its symbol. The letter is *always* capitalized. For example, the letter O stands for oxygen, H represents hydrogen, and S represents sulfur.



Pieces of aluminum cut from a pan and scraped clean with steel wool react with sodium hydroxide (left) and hydrochloric acid (right).

Identify the product on which this label may be found.

Aluminum is a commonly used, quite reactive metal.

Since there are only twenty-six letters in our alphabet and over 100 elements, the names of several elements begin with the same letter. In such cases, Berzelius suggested using the first two letters of the name of the element. Examples of this are Co, for cobalt; Ca, for calcium; Al for aluminum. Another method he suggested was to use the first letter of the name and a second letter whose sound is conspicuous when the name is pronounced. Examples of this are Cr, for chromium; Cl, for chlorine; and As, for arsenic. The first letter of the symbol is always capitalized regardless of which method is used, and the second letter is *never* capitalized.

For several elements the symbol is derived from other languages. The Latin name for iron is ferrum; the symbol for iron is Fe. Pb, the symbol for lead, comes from the Latin name, plumbum. The symbol for potassium is K, from the German word, kalium.

The significance of chemical symbols will become more apparent as your study of chemistry progresses.

2-9. LOOKING AHEAD

Thus far in our study of chemistry we have raised many questions. Before these can be answered satisfactorily, we must know something about the structure of atoms. Atoms are the fundamental particles that compose all elements. The atoms of each element are unique; they differ from those of other elements. In the next chapters we will study the development of ideas

that describe how these fundamental particles behave when they are in the company of other fundamental particles.

Suggestions for Creative Work

1. Devise an experiment to determine whether baking powder is a mixture or a compound.
2. Devise an experiment to show that sugar is a compound. Identify the products formed by decomposing sugar.
3. Mixtures of solids in solution can be separated by a process called fractional crystallization. Investigate this process and plan an experiment in which you separate potassium nitrate from copper nitrate when they are together in the same solution.
4. Grow large crystals of one or more of the following: alum, copper sulfate, table salt. Identify the crystal system to which each belongs.
5. Using a procedure similar to that used in Exp. 2-4, prepare a compound of copper and sulfur. How can you determine the best weights of copper and sulfur to use?

Suggestions for Creative Writing

1. Write an article on how the use of the methods of scientific investigation may be of help in daily activities.
2. Write a poem, using a concept introduced in Chapter 2 as a theme.

Practice Exercises *(Answers on pp. 309, 310)*

1. Classify the following properties as either physical or chemical:
 - a. Melts at 50°C
 - b. Occurs as a red powder
 - c. Burns in air
 - d. Oxidizes slowly
 - e. Dissolves in alcohol
 - f. Reacts with HCl
 - g. Density = 6.3 g/cc
 - h. Does not burn in air
 - i. Can be drawn into a wire
 - j. Supports burning
2. Classify the following changes as either physical or chemical:
 - a. Placing a 9-volt radio battery under water in which baking soda is dissolved
 - b. Cutting Al foil
 - c. Melting sulfur
 - d. Freezing water
 - e. Cooking an egg
 - f. Changing water to steam
 - g. Decay of wood
 - h. Burning magnesium ribbon
 - i. Dissolving salt in water
 - j. Crushing rock
3. From the following list of properties, select those which generally apply to metals:
 - a. Does not conduct heat
 - b. Has a luster
 - c. Is malleable
 - d. Conducts electricity
 - e. Is ductile
4. From the following lists of properties, select those which generally apply to gases:
 - a. Diffuses rapidly
 - b. Has definite volume
 - c. Shape not definite
 - d. Very compressible
5. Name the most abundant metal in earth's lithosphere and state its percentage by weight.

6. Apply the Law of Definite Proportions to explain the statement "Water is composed of 8 parts oxygen and 1 part hydrogen by weight."
7. Write the names of the following elements:
 - a. Na b. Hg c. K d. Cu e. Fe
8. Write the symbol for the following elements:
 - a. lead b. silver c. magnesium d. zinc e. tin
9. Explain the melting of paradichlorobenzene using the concepts of minimum energy vs. maximum randomness.
10. Explain the difference between Co and CO.
11. Two like magnetic poles are moved closer together to within a distance of 2 cm of each other. What change do you expect in the potential energy of this system? Give reasons for your answer.
12. A student collected data on the heating and cooling of a solid, using the same technique you used with paradichlorobenzene. When the data were plotted, it was found that there was a gradual rise in temperature throughout the melting process. No plateau occurred in the graph. Does this evidence indicate that the solid was a pure substance or a mixture? Give reasons for your answer.
13. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION	REASON
No significant change in temperature is observed during the melting of a pure substance.	Because the substance has reached its melting temperature.

Self-Test *(Answers on p. 310)*

1. Raw milk contains sugar, fat, and water. How could you demonstrate that milk is a mixture and that each of these substances retains its individual properties?
2. Cite evidence to indicate that water and sugar are compounds, but that a solution of sugar in water is a mixture.
3. Classify the following changes as either physical or chemical:
 - a. Tarnishing of silver
 - b. Magnetizing a needle
 - c. Heating aluminum foil
 - d. Igniting a flashbulb
 - e. Solid Dry Ice changing to a gas
4. Two colorless solutions are mixed and a yellow solid appears. What kind of change is this? Give reasons for your answer.
5. Name the most abundant nonmetal in earth's lithosphere and atmosphere and give its percentage by weight.
6. A student heated 3 g of sulfur and 3 g of iron in a test tube. After all evidence of chemical action had stopped, he examined the contents of the test tube. Which element do you predict he found partially unreacted? Assuming that 7 g of iron and 4 g of sulfur react completely, calculate the weight of the element this student found in excess.
7. Two unlike magnetic poles are moved from a distance of 20 cm to a distance of 10 cm. What change do you expect in the potential energy of the system? Give reasons for your answer.

8. Write the symbols for the following elements:
a. manganese c. chlorine e. nickel
b. tungsten d. calcium
9. Write the names for the following elements:
a. F b. Au c. He d. N e. C
10. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION

If you push two magnets together with *like* poles facing and then let them go, they will move apart.

REASON

Because kinetic energy is changed to potential energy.

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Chapter 5 on "Accounting for Three States of Matter" employs the kinetic theory. Easy reading and very informative.

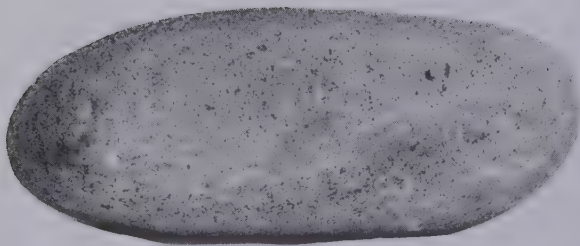
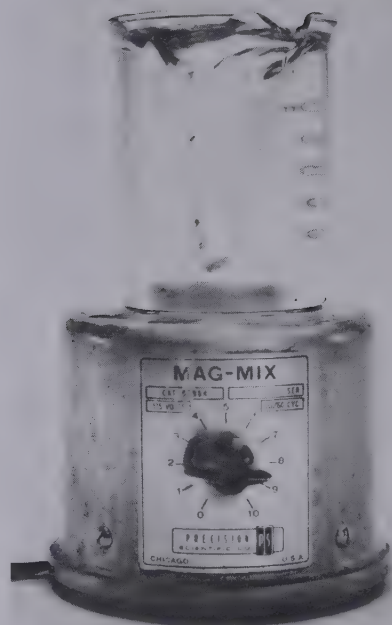
Ingredients: Water, sugar syrup, concentrated skim milk, food starch modified, vegetable oil mono- and diglycerides, salt, artificial flavor, artificial color

Ingredients:

Sugar, hydrogenated coconut and soybean oils, propylene glycol monostearate (emulsifier—for uniform blending of oil), lactose (milk sugar), sodium caseinate (a protein), whey solids, sodium silicoaluminate (prevents caking), hydroxylated soybean lecithin (emulsifier), artificial flavor and color, BHA (a preservative).

113 gm.







PROPERTIES OF LIQUIDS AND THE SOLUTION PROCESS

OBJECTIVES:

By the time you have completed your study of liquids and solutions, you will be expected to demonstrate acceptable performance on the following objectives.

1. *Explain* the differences between solids, liquids, and gases in terms of shape, volume, compressibility, and intermolecular space.
2. *Apply* Le Chatelier's Principle to predict the effect in changing the temperature, pressure, volume, or amount of reacting material on the following equilibrium systems: (a) liquid-liquid, (b) liquid-gas, (c) solid-liquid, and (d) solid-gas.
3. *Apply* the concepts of kinetic energy and molecular attraction to explain why water is most dense at 4° C and why either raising or lowering the temperature causes a decrease in water density.
4. *Recognize* an equilibrium system and a steady state system, given samples of each.
5. Given a list of liquids with their vapor pressures, *predict* whether their boiling temperature will be high or low.
6. *Apply* your knowledge of the properties of water to explain the seasonal turnover in large lakes.
7. Given a metal and access to the usual laboratory equipment, *determine* what products are formed when the metal is placed in water.
8. *Apply* the principles of kinetic and potential energy to explain why a steam burn is more severe than a boiling water burn when both the steam and the water are at a temperature of 100° C.
9. *Explain* the phase change from liquid to vapor, using the concepts of minimum energy and maximum randomness.
10. *Describe* the three general steps in the solution process and *state* how we determine whether the process is endothermic or exothermic.
11. Given a sample of liquid, *determine* whether it contains a dissolved solid.
12. *Recognize* a solution when given a set of liquid-solid mixtures.
13. *Describe* how to prepare a solution of a specific molarity, given the formula of the solute and the atomic weights of the component elements.
14. *Apply* Le Chatelier's Principle to predict the effect of temperature change on an equilibrium system of (a) solid in water and (b) gas in water.
15. *Apply* the concepts of minimum energy and maximum randomness to explain the dissolving of (a) solids and (b) gases in water.
16. Given a solid, *determine* whether it dissolves endothermically or exothermically.
17. Given a graph showing the number of grams of solute which dissolve in 100 grams of water at various temperatures, *determine* for a saturated solution the number of (a) grams and (b) moles of solute which will dissolve in 100 grams of water at a stated temperature.

SUGGESTED ORDER OF STUDY

1. Perform Exp. 3-1. Hand in formal report. ✓
2. Study Secs. 3-1 through 3-3.
3. Perform Exp. 3-2. Hand in formal report. ✓

4. Study Secs. 3-4 and 3-5 through "Molecular Structure of Matter."
5. Perform Exp. 3-3. Hand in formal report. ✓
6. Complete study of Sec. 3-5.
7. Perform Exp. 3-4. Hand in formal report. ✓
8. Study Secs. 3-6 through 3-9.
9. Perform Exp. 3-5. Hand in formal report. ✓
10. Study Secs. 3-10 through 3-15.
11. Plan creative work; do creative writing; explore activities related to the chapter.
12. Review chapter as needed. Take Self-Test. Review further if needed.
13. Take test for Chapter 3.

3-1 · PROPERTIES OF THE LIQUID STATE

You have observed that when a lump of sugar is dropped into a beaker of water, the sugar gradually disappears. We say the sugar dissolves in the water. This causes the water to taste sweet. Such a mixture of a solid in a liquid is called a solution. The dissolved sugar cannot be removed by filtering, nor can the sugar particles be seen even with a microscope. However, if the water is evaporated, the solid sugar can be recovered.



Where does the sugar go as it dissolves?

Since most common solutions consist of a solid dissolved in a liquid, we need to study the properties of liquids before we can understand the solution process. The most common liquid is water.

Remember that matter can be classified as solid, liquid, or gas. In solids the particles are close to each other and the substance maintains a definite shape. In most liquids the particles are somewhat farther apart. In gases the particles are widely separated; they touch only when they collide. The follow-

ing properties are generally characteristic of liquids:

1. *Definite volume.* Liquids have a definite volume and do not expand to fill all the space in a container as gases do.
2. *Indefinite shape.* Liquids flow and can be poured from one container to another. In every instance the liquid takes on the shape of the container into which it is poured.
3. *Incompressible.* Even though the particles in a liquid have freedom of motion, they are almost as close together as they can get at room temperature. This means that at ordinary temperatures the liquid cannot be compressed very much. If you have ever done a "belly-buster" while learning to dive, you know from experience that water does not compress easily.
4. *Diffuse slowly.* The mixing, or diffusion, of liquids is very slow. You observed this property of liquids in Exp. 1-4. The layer of potassium permanganate solution in the bottom of the test tube at room temperature mixed very slowly with the water above it. This is because the particles in the liquids are quite close together, and any given molecule will collide with many other molecules while making its way through the liquid. There is not much open space available through which any given particle can move, and this slows its progress through the liquid.
5. *Evaporate at room temperature.* Water and many other liquids will change into the gaseous state at room temperature. Some liquids evaporate more rapidly than others. Propose a hypothesis to explain this fact. What are some factors that might affect the evaporation rate of a liquid?

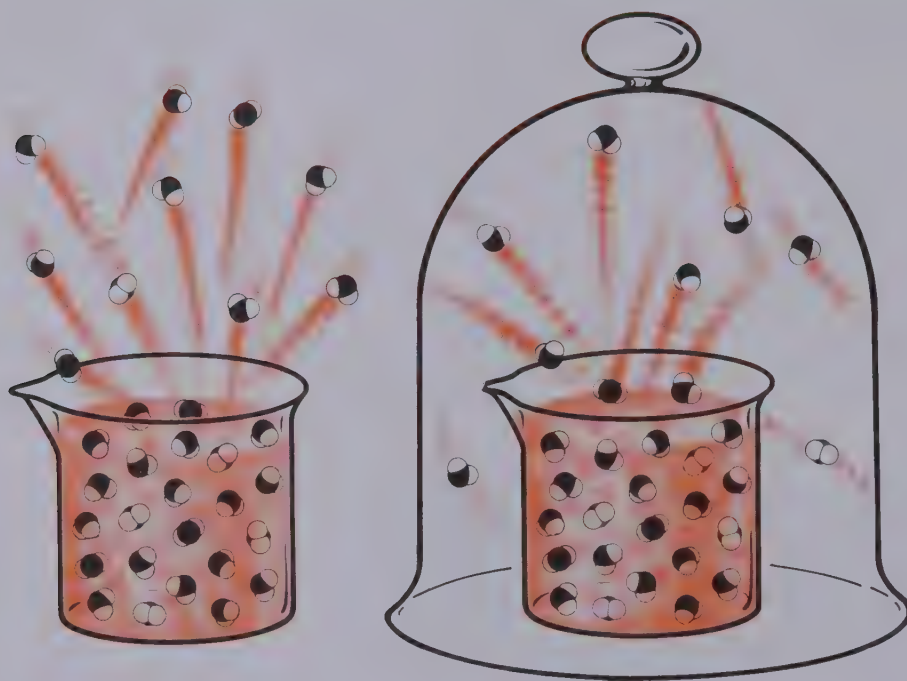
3-2. EVAPORATION OF LIQUIDS

The space between the molecules in a liquid is small. Because the molecules are close together, their attraction for one another is relatively great. This accounts for the fact that a given sample of a liquid maintains a constant volume. Ten cubic centimeters of water poured from a graduated cylinder will occupy only 10 cc of space in a 500-cc beaker or in a 1-liter container. The forces of attraction between the molecules are great enough to confine the molecules to a constant volume.

But the fact that liquids evaporate indicates that the attractive forces between the molecules can be overcome. How can this be explained? You might measure the temperature of a beaker of water and find it to be 20° C. This is an indication of the average kinetic energies of *all* the water molecules in the beaker. However, individual molecules in the sample will have many different kinetic energies. Even if it were possible to begin with a sample of water in which every molecule had exactly the same kinetic energy, their energies would soon vary. This is because they are constantly colliding with one another. In any collision, one molecule may gain energy while the other molecule loses energy. If a high-energy molecule near the surface of a liquid collides with another molecule, it is possible for it to gain sufficient energy to overcome the attractive forces of the surrounding molecules and escape from the liquid into the gaseous state. Since the molecules with high kinetic energy

are the ones that escape from the liquid, this means the remaining ones have lower average kinetic energy. Let us use an analogy: If you remove the fastest boy from the track team, this reduces the average speed of the team. The speed with which the remaining boys can run has not been changed, but the average speed of the team has been reduced.

If you have a 100-cc sample of water at a temperature of 20° C and another 100-cc sample of water at 70° C, which would evaporate faster?



Does evaporation occur at the same rate in both situations?

Evaporation in a Closed System

In Exp. 3-1 you obtained evidence that although evaporation goes on in a closed system, there comes a time when evaporation appears to stop. Soon after the liquids are placed in the sealed containers, the more energetic molecules begin to escape from the liquid into the gas phase (state). Occasionally, some of the gaseous molecules return to the liquid phase; this is called *condensation*. After awhile, the rate at which molecules are escaping from the liquid equals the rate at which they are returning to it. We say that the rates of evaporation and condensation are equal. When these two processes occur *at the same time and at equal rates in a closed system, equilibrium is established.*

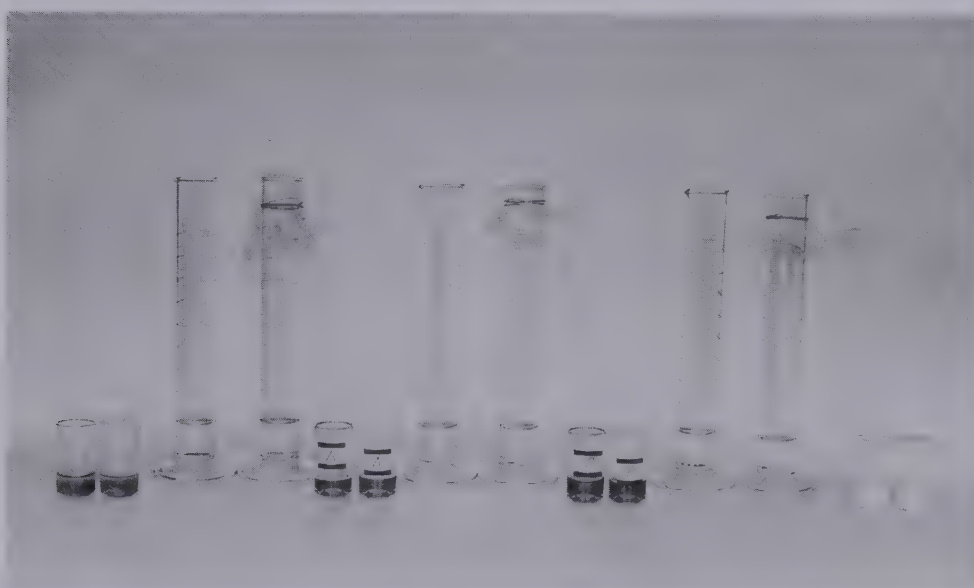


We recognize an equilibrium system by the fact that no *visible* changes are occurring. However, we must remember that at the molecular level there

is a great deal of activity among the particles. For this reason, such a system is said to be in *dynamic equilibrium*. Dynamic equilibrium can occur only in a closed system in which none of the molecules are leaving the system. You will recall that in the tubes that were not sealed, evaporation continued until all the liquids were entirely gone.

3-3· EQUILIBRIUM VERSUS STEADY STATE

The sealed tubes of liquids in Exp. 3-1 provide evidence for the three conditions necessary for an equilibrium system: (1) the system must be closed; that is, the amount of matter in the system must remain constant; (2) the system must be at constant temperature; and (3) the visible properties of the system must be unchanging. In the open containers, gaseous molecules were leaving the tubes and escaping into the air in the room. Equilibrium could never be established under these conditions because only a few of the gaseous molecules had an opportunity to return to the liquid phase.



In which graduated cylinders does equilibrium exist? Does a steady state exist in any of them?

An analogy which may help to make this concept of equilibrium clearer can be drawn from a football game. The coach may have thirty boys on his squad, but only eleven are permitted on the playing field at any given time. As one boy leaves the game to return to the bench, a player from the bench "escapes" onto the playing field to take his place. The rate at which players leave the bench is always equal to the rate at which players return from the field. Throughout the game only boys who are on the squad may enter or leave the game, so the amount of "matter" in this system is constant.

This analogy is in contrast to a line of students in the cafeteria. A casual observer might look at the line several times during the lunch hour. It would always *appear* to be the same, but students are constantly leaving the line and being replaced by *different* persons. The "matter" in this case is continually



Consider whether the above three systems are examples of steady states or equilibriums.

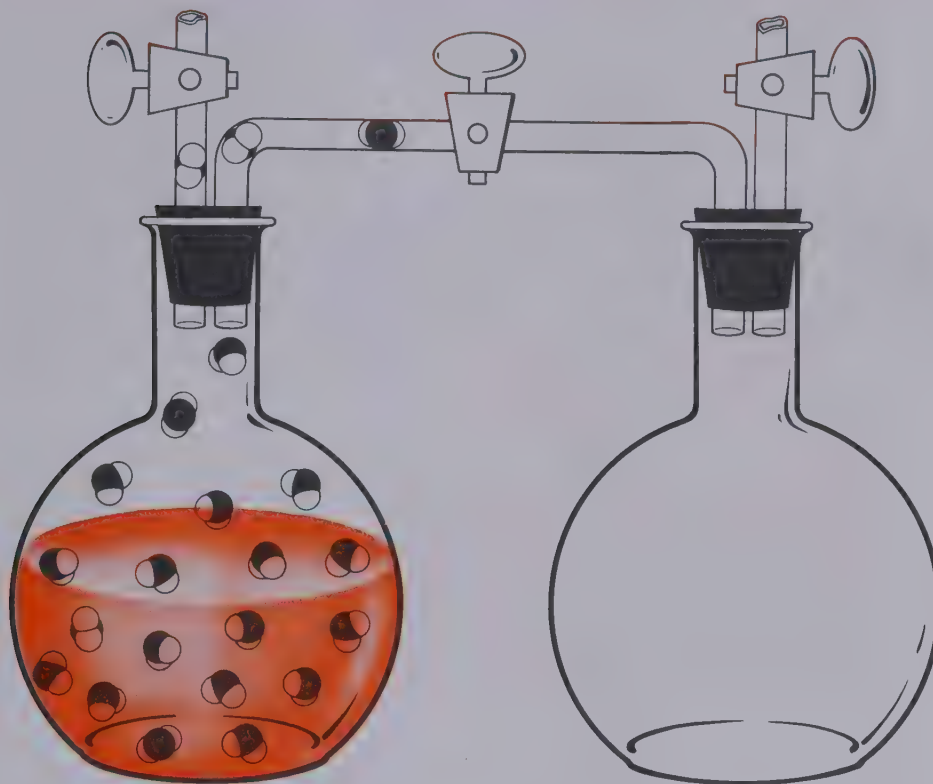
changing, and we do not have an equilibrium system. We call this a *steady state*. The bunsen burner flame represents a steady state because, as fuel is burned, new fuel is fed into the system. The products of combustion, water and carbon dioxide, are leaving the system. Equilibrium would never be established under these conditions.

Le Chatelier's Principle

The concept of equilibrium is one of the most useful and important ideas in the study of chemistry. Henri Louis Le Chatelier (1850–1936) was Professor of Chemistry at the Ecole Des Mines (School of Mines) in Paris, France. He was trained as a mining engineer, and throughout his career he was particularly interested in applying scientific principles to industrial purposes. This led to the discovery for which he is best known: Le Chatelier's principle of

equilibrium. This principle states that *if a system at equilibrium is disturbed, changes occur in the system that tend to offset the disturbing factor until a new equilibrium is achieved.*

For example, in the equilibrium liquid-vapor systems in Exp. 3-1, if you suddenly increased the volume of a cylinder, evaporation would proceed



What will happen when the valve between the two flasks is opened?

faster than condensation for a while. Eventually, gaseous molecules would again be returning to the liquid state at the same rate as molecules are leaving it. If you decreased the volume of the container, condensation would occur at a more rapid rate than evaporation until a new equilibrium was established. Then under the new equilibrium conditions, evaporation and condensation would once again go at equal rates.

We will apply Le Chatelier's principle of equilibrium to explain many observations during our study of chemistry.

3-4. THE BOILING POINT OF LIQUIDS

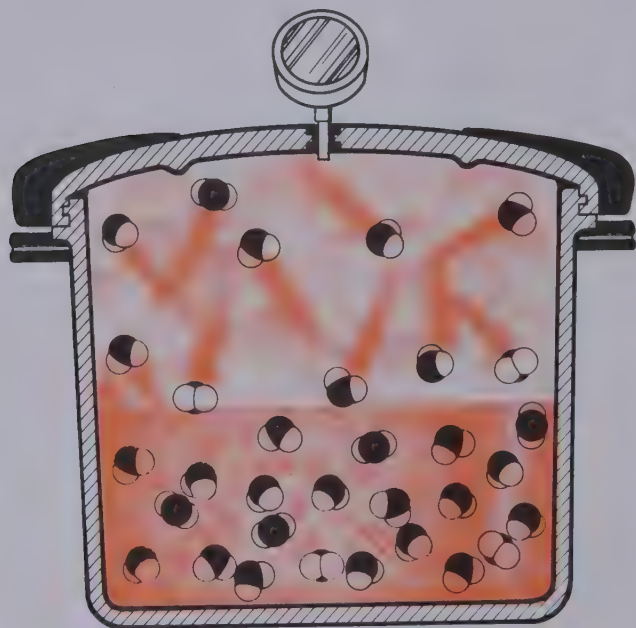
When water evaporates in a closed system, the gaseous molecules mingle with the air molecules which are already present above the liquid. This causes an increase in the pressure on the remaining liquid. At equilibrium the part

of this total pressure which is caused by the gaseous water molecules is called the *equilibrium vapor pressure*. We can represent these statements by two equations:

pressure of air molecules + pressure of gaseous water molecules
= total pressure on the liquid

pressure of gaseous water molecules = equilibrium vapor pressure

The equilibrium vapor pressure increases as the temperature of the liquid is raised. Every liquid has its own characteristic vapor pressure at room tem-



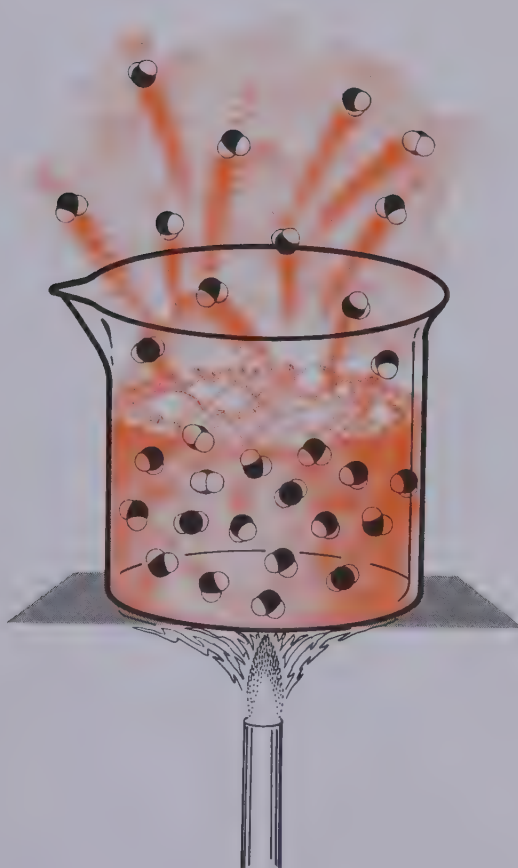
What happens to the evaporation and condensation rates inside the pressure cooker as the temperature rises?

perature. The vapor pressure for different liquids varies because the attraction between molecules varies. Water molecules have a much greater attraction for each other than do the molecules of carbon tetrachloride. At 20°C , the vapor pressure of water is 17.5 torr, while at the same temperature, the vapor pressure of carbon tetrachloride, CCl_4 , is 91.0 torr. (In these pressure units, standard atmospheric pressure at sea level is 760 torr.) The higher the vapor pressure of a liquid, the more readily it will evaporate at room temperature.

As the temperature of a liquid is raised in an open container, the pressure of the escaping vapor increases until it equals the atmospheric pressure. The temperature at which the vapor pressure of a liquid equals that of the atmosphere is known as the *boiling point* of that liquid.

Energy Changes at the Boiling Temperature

You have noticed that when water boils, the temperature of the liquid does not rise as long as both liquid and vapor are present. Even though heat is added continuously, the temperature of the liquid remains constant. This means that the average kinetic energy of the molecules is constant. What is happening to the added energy?



Compare the potential energy of the gas molecules with that of the liquid molecules.

You already know that extra energy is needed to overcome the force of attraction between two magnets; work must be done to separate them. Similarly, in order to convert a liquid to its vapor state, energy must be added to overcome the attractive forces between the molecules. As heat energy is added, the *potential* energy of the system increases. Approximately 540 calories of heat are required to convert each gram of liquid water to a gram of water vapor at the boiling point. This quantity of heat is called the *heat of vaporization* of water.

When the temperature of the boiling water and that of the water vapor are the same, the average *kinetic* energy of the molecules in both states is the same. However, since each gram of the water vapor has 540 more calories of heat in it than a gram of boiling water, steam causes more severe burns than water at the same temperature. The extra heat is stored as potential energy, and when the steam condenses on your skin, this 540 calories per gram is released as heat.

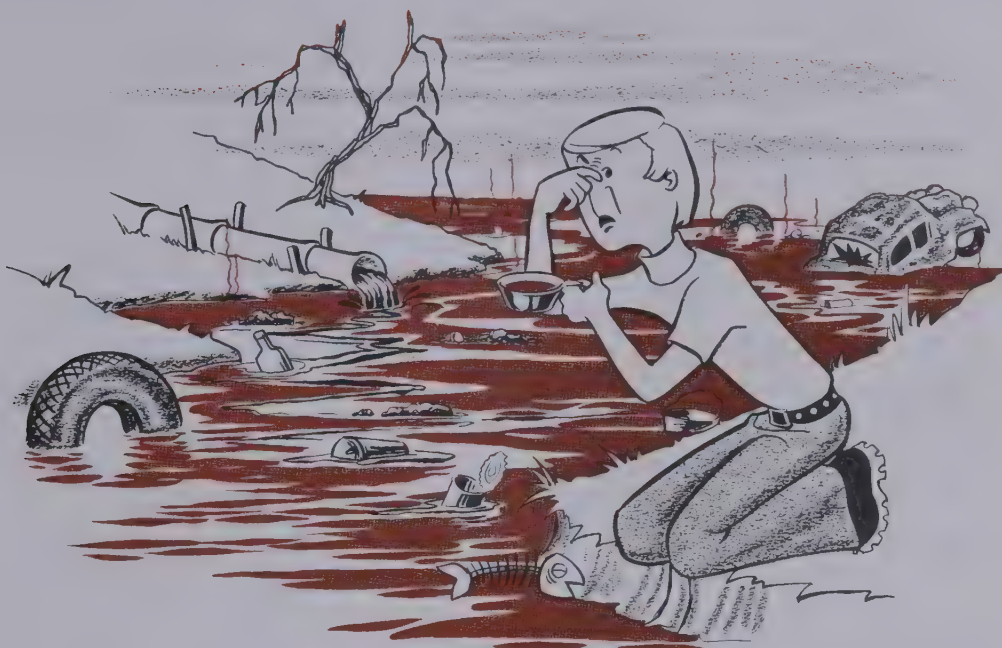
Does the temperature of melting ice remain constant during the change of state? Is the potential energy of liquid water at 0°C greater or less than that of ice at 0°C ? Devise an experiment to help you answer these questions.

Randomness versus Energy

How do the opposing tendencies of maximum randomness and minimum energy apply when a liquid vaporizes? In the liquid state, water molecules are in motion, but they are close enough together so that their potential energy is low. The temperature of the water indicates the average kinetic energy of the molecules. As heat energy is applied and the temperature of the water increases, the kinetic energy of the molecules increases. This enables some of the higher-energy molecules to overcome the attractive forces of the liquid and escape as gaseous molecules. Randomness is greatly increased because gaseous molecules are much farther apart and there are many more ways in which they can be arranged. The potential energy of the molecules is also increased. If the liquid and gaseous states are at the same temperature, then the average kinetic energy of the two states is the same. Only the potential energy has increased. Maximum randomness is gained at the expense of the work necessary to increase the potential energy.

3-5. WATER IS AN UNUSUAL LIQUID

Water is such a familiar part of your environment that you may not be aware of just how unusual it is. It is necessary to sustain life as we know it. It makes up about two-thirds of your body weight and as much as 98 percent of the weight of certain plants. Evaporation of water helps regulate your body temperature. Many of the chemical processes in both plants and animals occur in water solutions. Water covers about three-fourths of the earth's surface and exerts an important effect upon climate. The tremendous importance of water is largely due to its unique properties.



Can this stuff really be odorless, tasteless, and colorless?

Physical Properties of Water

Pure water is colorless, odorless, and tasteless. Any odor or taste in water is caused by dissolved minerals or gases. Water can exist in any of the three physical states: solid (ice), liquid, or gaseous (vapor). At one atmosphere of pressure (760 torr), pure water freezes at 0° C and boils at 100° C. At most locations at altitudes above sea level the pressure is usually not 760 torr (except perhaps once or twice a year, at most). Usually the pressure is less than 760 torr. So, water usually boils at a temperature less than 100° C.

The changes that take place in the density of water as its temperature changes are very unusual. No other common liquid is like water in this respect. Most liquids increase in density as the temperature is lowered, until they reach their freezing points. Water does not follow this pattern. As the temperature of water is lowered, the density increases until it reaches 4° C. At this temperature one cubic centimeter of water weighs one gram. The density is 1.0 g/cc at 4° C. Further cooling causes water molecules to move apart, thus *decreasing* its density. This decrease in density continues until water freezes at 0° C. During the freezing process the volume of the water increases about nine percent and the density decreases to 0.92 g/cc.

This unusual property of water explains why large lakes do not freeze throughout, but only from the top down. So long as the water surface is above 4° C, cooling of the surface *increases* its density. This causes the surface water to sink, and the movement sets up convection currents that tend to equalize the temperature throughout the body of water. When the surface water reaches

$$d = \frac{m}{v}$$

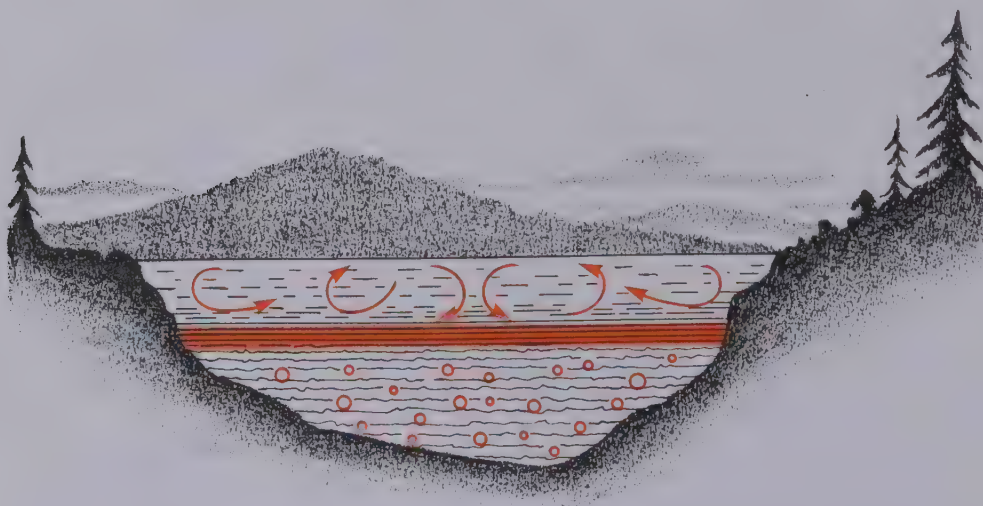
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$$t \downarrow$$

a temperature of 4°C , further cooling *decreases* the density and keeps the water from sinking, so freezing can occur only at the surface. This is a great advantage to plant and animal life in the water because even in a very cold winter, it is highly unlikely that the lake or pond would freeze completely solid. Of course, in shallow pasture ponds one might expect complete freezing if the weather remained below 0°C for extended periods of time.

Seasonal Turnover in Large Lakes

Another interesting result of this unusual density change in water should be mentioned. During the summer the top region of a large body of water becomes much warmer than the lower region. This results in the two regions becoming sufficiently different in density that they cease to mix. This produces a separation into layers. The warm top layer continues to circulate, but does not mix with the more dense layer deep in the lake. In the depths of a large body of water the temperature remains at 4°C all the time. Either warming or cooling would cause it to become less dense and to rise. But during the summer the cold layer does not circulate because there is very little change in its density. This causes the oxygen supply to become depleted and waste gases to accumulate, greatly affecting life in this part of the lake.



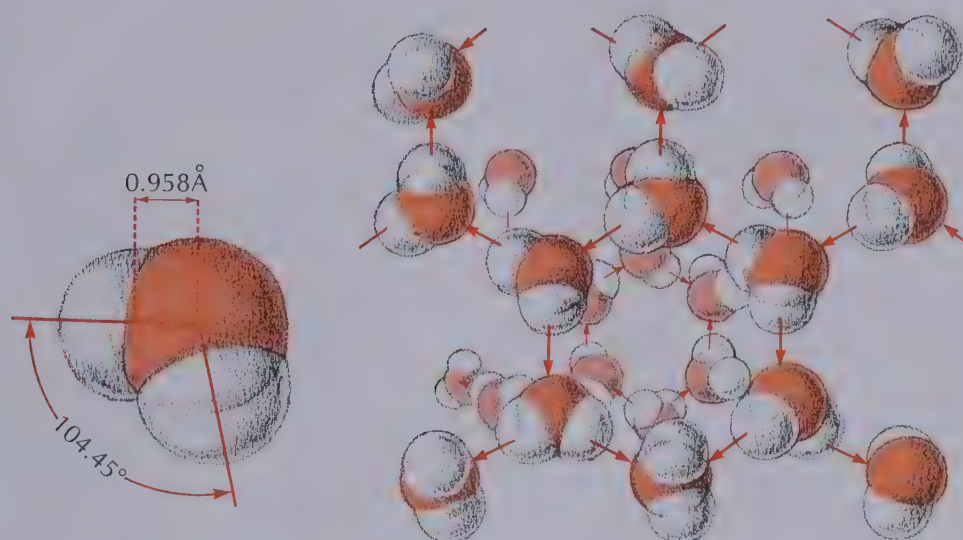
In large lakes in summer the warm top layer does not mix with the more dense cold layer.

As cooler weather comes in the fall, the top layer cools until the density is comparable to that in the lower region and once again total circulation begins. This phenomenon is known as the "fall turnover" and may be evident in both the odor and taste of the water. As total circulation begins, the accumulated gases escape into the air over a period of several days.

Molecular Structure of Water

What causes water to be so different from other liquids? Water molecules are

composed of one atom of oxygen and two atoms of hydrogen. According to the best information we have, the region of the molecule around the oxygen atom is somewhat negatively charged, which leaves the regions near the hydrogen atoms somewhat positively charged. Further, a water molecule is bent; the angle between the bonds joining the hydrogens to the oxygen is about 105° . We can represent the structure of a water molecule like this:



A scale model of the water molecule showing the bond angles and relative sizes of the oxygen and hydrogen atoms and an exploded representation of the arrangement of water molecules in an ice crystal.

The structure of the water molecule will be studied in greater detail in Chapter 10. For the present, this description may help you to understand why water molecules have a great attraction for one another. One of the positive ends of one molecule is attracted to the negative part of a nearby molecule much as the unlike poles of a magnet attract each other. These attractive forces make the water molecules difficult to separate and they also account for the low vapor pressure of water. This means that a great deal of heat energy must be put into the water to bring it to the boiling point. When several water molecules become attracted to their neighbors, as water at 4°C is cooled further, open spaces are formed, and the density of the water decreases.

Chemical Properties of Water

In Exp. 3-3 you observed the reaction between water and a metal, a metallic oxide, and a nonmetallic oxide. The chemical properties of water can be summarized as follows:

1. *Behavior with metals.* Calcium, sodium, and potassium metals react with cold water to produce free hydrogen gas and a *hydroxide*. Hydroxides are compounds that release OH^- ions in solution and cause litmus to turn blue; they are commonly called *bases*. The properties of bases will be considered in Chapter 4.



An example of a metal, sodium, reacting with water to form hydrogen gas and a hydroxide.

2. *Behavior with metallic oxides.* The oxides of calcium, sodium, and potassium also react with water to produce a base, or hydroxide.
3. *Behavior with nonmetallic oxides.* The oxides of carbon and sulfur react with water to form *acids*. Acids turn litmus red. Their properties will be studied in Chapter 4.
4. *Water is very stable.* Water molecules are extremely stable; that is, it is very difficult to break the bonds holding the oxygen and hydrogen atoms together. One satisfactory method for decomposing water molecules is to pass an electric current through the water. When we do this, we obtain oxygen gas at the positive electrode and hydrogen gas at the negative electrode.
5. *Water is necessary for many chemical changes.* Often when dry chemicals are mixed, we can see no evidence of change. But when water is added to the mixture, there often is evidence of chemical change. The importance of water in promoting chemical changes will become more apparent as we study the nature of solutions.

3-6. INTRODUCTION, TO SOLUTIONS

In our study of liquids we were primarily concerned with pure substances. However, in daily living we encounter mixtures far more frequently than any other type of matter. We live in a mixture of gases; the foods we eat are mixtures; even the water we drink is a special kind of mixture. Mixtures may be heterogeneous or homogeneous. Heterogeneous mixtures consist of distinct phases whose properties remain more or less well defined. Homogeneous mixtures, on the other hand, consist of a single phase whose properties may be considerably different from those of its components. *When a mixture is homogeneous, we call it a solution.*

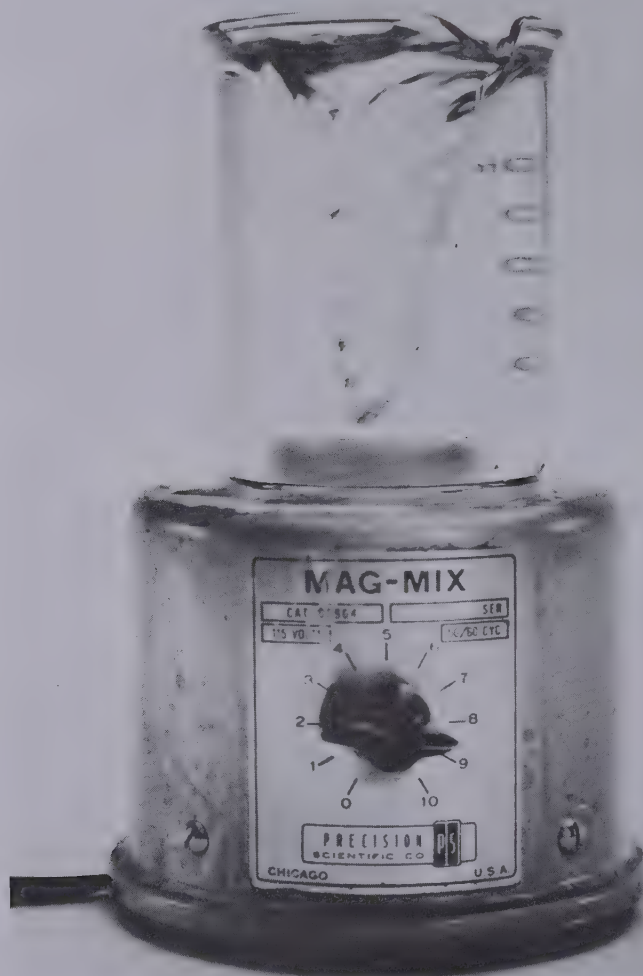


Water solutions and their effects are to be found everywhere on the earth.

Most of the physical and chemical processes that are necessary to sustain life occur in water solution. The majority of chemical reactions that occur in the laboratory and in industrial processes also occur in solution. Even in geological and biological processes, the predominant medium of activity is in liquid solution. Therefore, it is important that we learn about the nature of solutions.

3-7. GENERAL PROPERTIES OF SOLUTIONS

In Exp. 1-1 you prepared a solution, although you may not have been aware of it. You placed a sugar cube in water and observed it until you could no longer see the particles. Such a homogeneous mixture containing more than one substance is a solution. Most of the solutions with which we are concerned consist of a solid dissolved in water. It is convenient to refer to the parts of a solution as the solvent and the solute. The substance present in largest amount is the *solvent*, and the substances present in smaller amounts are each called *solutes*. In the broad concept, a solution is a homogeneous dispersion of two or more kinds of substances.



A magnetic stirrer is an extremely handy device to use when preparing laboratory solutions.

In general, water solutions are characterized by the following properties. The solute particles:

1. Are uniformly distributed throughout the solvent.
2. Are molecular in size and cannot be seen.
3. Cannot be removed by filtering.
4. Do not settle out on standing.
5. Form a transparent mixture, whether colorless or colored.

These properties will serve as guidelines in helping you to decide whether or not a solution exists as you proceed with your laboratory work.

3-8. CLASSIFICATION OF SOLUTIONS

Solutions may be composed of any combination of the three physical states of matter. Therefore, nine classes of solutions are possible. The solvent may be a solid, a liquid, or a gas; and the solute may be a solid, a liquid, or a gas.

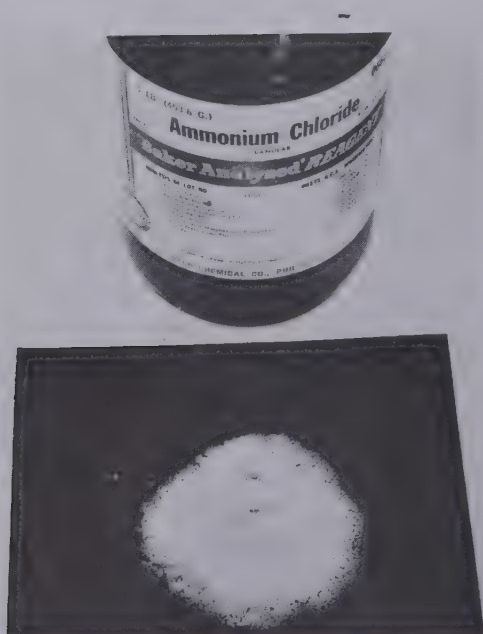
Classes of Solutions			
Physical State of Solution	Solute	Solvent	Examples
1. Gaseous	1. Gas	In Gas	Air; any mixture of gases
	2. Liquid	In gas	The evaporation of water into air
	3. Solid	In gas	The disappearance of dry ice upon standing
2. Liquid	4. Gas	In liquid	Oxygen in water; ammonia in water
	5. Liquid	In liquid	Alcohol in water
	6. Solid	In liquid	Sugar in water; iodine in alcohol
3. Solid	7. Gas	In solid	Hydrogen in palladium
	8. Liquid	In solid	Dental amalgams; mercury in gold
	9. Solid	In solid	Some alloys, such as copper in nickel; candle wax

Table 3-1

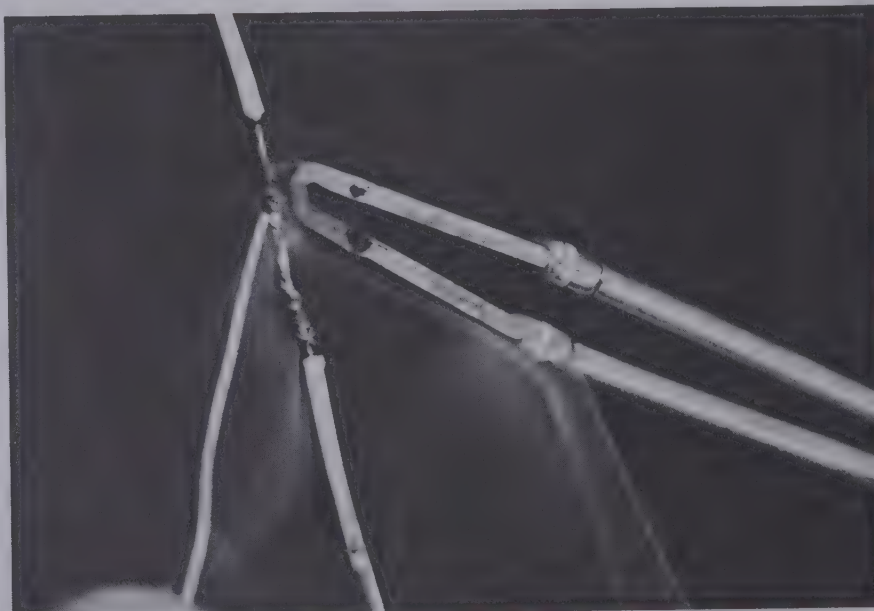
Of course, there are many combinations of substances that cannot form solutions. Gasoline will not dissolve in water; we say that these two liquids are *immiscible*. Gasoline will dissolve in motor oil to make a homogeneous solution; we say that these two liquids are *miscible*. Alcohol and water are miscible, as you can see from the example in Table 3-1. Some solids will not dissolve in some liquids. Sand will not dissolve in water; we say that sand is *insoluble* in water. Sugar is soluble in water and iodine is soluble in alcohol, as you can see from Table 3-1.



What different solutions can you identify with this picture?



What might happen to a solid like ammonium chloride if it is left exposed to the air?



Solder is a low melting-point alloy of lead and tin. Is it a solution?

Copper metal will dissolve in silver metal when both are liquids, at high temperatures. But as the mixture cools and solidifies, the metals become insoluble. Sterling silver is a mixture of about 8 or 9 percent copper and 92 or 91 percent silver.

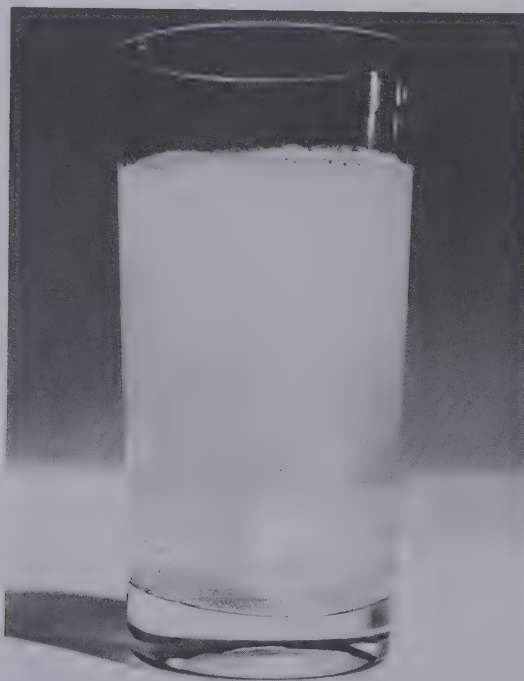
Instead of using words like soluble, insoluble, miscible, and immiscible, it is more practical to say dissolved state or dispersed state. Whenever a solution is formed to make a homogeneous mixture, the particles of one substance are dispersed, or dissolved, among the particles of the other.

3-9• THE NATURE OF THE SOLUTION PROCESS

If you take a careful look at an Alka-Seltzer tablet, you see no evidence of any reaction taking place. However, if you drop the tablet into a glass of water, a very rapid reaction occurs. The addition of water causes the crystals to dissolve, and the dissolved crystals react in the solution. Just what is the nature of the solution process?



Cooking oil (top) and water (bottom) are immiscible in each other.

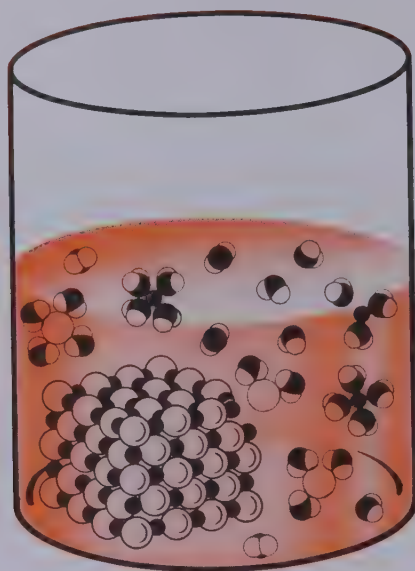


An Alka-Seltzer tablet dissolving in a glass of water.

The solution process is complex and is not completely understood at the present time; there are certain aspects of the process however, upon which chemists agree.

When an Alka-Seltzer tablet dissolves, the crystals dissociate into charged particles called *ions*. On the other hand, when sugar dissolves in water, it separates into particles called molecules, which are not charged. In some cases, a solution may be composed of a mixture of both ions and molecules. In all cases, when a solute is dissolved in a liquid, its particles are not closely packed, but are free to move about in a random fashion. This means that when a solute is placed in water, or in any liquid solvent, there is opportunity for the solute particles to collide with solvent particles.

The solid state of matter is characterized by less potential energy than the liquid or dissolved state. In solid sodium chloride, for example, positively charged sodium ions and negatively charged chloride ions have great attraction for each other and, like the magnets you studied in Exp. 2-5, they have the lowest potential energy when these unlike charges are close together. Energy must be supplied and work must be done to pull these unlike ions away from each other.



A model depicting the dissolving of sodium chloride in water.

When an ionic solid is placed in water, the positive and negative parts of the water molecules attract both kinds of charged ions away from the other ions in the crystal, and we say the solid dissolves. As the ions become dispersed in the water, negative ions attract the positive ends of some water molecules; positive ions attract the negative ends of other water molecules. We visualize each ion as being surrounded by water molecules. When this happens, energy is released because once again unlike charges are close together. This ion-water molecule attraction is called *hydration*, and the energy released as a result of this process is known as *hydration energy*.

Water molecules are said to be polar; the word *pole* signifies two opposites, such as the North Pole and South Pole of the earth, or the positive (two) and negative (one) ends of water molecules. The dissolving of salt in water is a process in which the polar molecules of the water become attached to the charged ions, releasing hydration energy.

We can summarize the steps in the solution process in this fashion:

1. Solute particles are separated from the crystal when they absorb sufficient energy.
2. Solvent particles move apart to provide space for the solute particles.
3. Solute particles are attracted to solvent particles with a resulting release of energy.

Thus, we can see that step 1 is endothermic and step 3 is exothermic. Does the addition of a solute to water cause a rise or a drop in the water temperature? For most solids, the *net* effect is endothermic. That is, more energy is absorbed in step 1 than is released in step 3.

It should be apparent that the stronger the bonds holding the solute together, the more difficult it will be to attract them away from the crystal; the weaker the bonds between the ions, the easier it will be to cause them to separate. Does the bond type of the solvent have any effect on the dissolution of a given solute? You can answer this question in the laboratory during your study of Chapter 7.

3-10. CONCENTRATION OF SOLUTIONS

The more solute that you dissolve in a solution, the *more concentrated* the solution. If you dissolve ten sugar cubes in 250 cc of water, the solution is more concentrated than if you dissolve only one sugar cube in that volume of water. Conversely, if you add 100 cc of water to the solution containing only one sugar cube, you have a *dilute* solution. We can increase the concentration of a solution by adding more solute, or by evaporating some of the solvent.

The terms *concentrated* and *dilute* are qualitative and can be used only in a very general sense. Since the properties of solutions depend upon the relative amounts of solute and solvent, the chemist uses more quantitative methods to express the concentration of solutions.

Molar Solutions

The most generally used expression for indicating the concentration of solutions gives the quantity of solute in *moles* and the volume of the solution in *liters*. This is called *molarity* and is designated by the capital letter M.

Volumetric flasks provide a handy way to prepare fixed amounts of solutions of specified concentration. The quantity in the reagent bottle to the right of each flask represents the amount of ammonium dichromate necessary to make a 0.1 molar solution using that flask.



A *one-molar* (1-M) solution is one that contains one mole of solute per liter of solution. We will consider the meaning of a mole in greater depth later, but for our present purposes it is sufficient to know that the number of grams in a mole can be determined from the formula for a substance with the aid of a table of atomic weights, such as the one in Appendix 12. Using the formula for a substance, we can look up the atomic weights of the elements in the formula and add these together. The sum of the atomic weights is called the *formula weight* (or the *molecular weight*, if the substance forms molecules). The formula weight, expressed in grams, is the weight of a mole of the substance.

Suppose that we wished to make a one-molar solution of potassium chloride, KCl. How would we go about it? First, we need to know how much one mole of KCl weighs. We get this information from a table which lists the weights of a mole of atoms, the so-called atomic weight table, in Appendix 12. In that table, the atomic weight of potassium is shown as 39.1. This means that a mole of potassium atoms weighs 39.1 grams. Similarly, the atomic weight of chlorine is 35.5; the weight of a mole of chlorine atoms is 35.5 grams. So we add:

$$\begin{array}{r} 39.1 \text{ grams} \\ 35.5 \text{ grams} \\ \hline 74.6 \text{ grams} \end{array}$$

A mole of potassium chloride units weighs 74.6 grams. To make a 1.0 molar solution, we would dissolve this much potassium chloride in enough water to make a liter of solution. For this, a special flask called a *volumetric flask* is often used. It has a mark on the neck which indicates exactly how full it is to be filled, to hold, say, 1 liter of liquid. So, the steps are:

1. Determine the weight of one mole of the solute in grams using the table of atomic weights, and adding these to get a sum.
2. Place the weighed solid in a 1-liter volumetric flask with a small amount of water.
3. Swirl to hasten the solution process. Add a *little* more water if necessary to get the solid to dissolve, and swirl some more.
4. Add enough more water, carefully, to get the *total volume* of solute (the solid) and solvent (water) to the line marked on the neck of the volumetric flask.
5. Stopper the flask and turn it upside down and right side up several times to mix well. Be sure the stopper does not fall out as you do this.

Suppose a 0.5 molar solution were needed. Add one-half the weight of a mole as the quantity of solid solute to be weighed out. Suppose a 2.0 molar solution were desired. Use twice the weight of a mole of solute. When 1 liter of solution is desired, this is the *total amount of solute and solvent* that equals 1 liter. Do not add 1 liter of solvent. For other volumes of solution, a comparable precaution applies.

Problems:

1. How many grams of sodium iodide, NaI, would be needed to prepare 1 liter of a 0.5 molar solution?

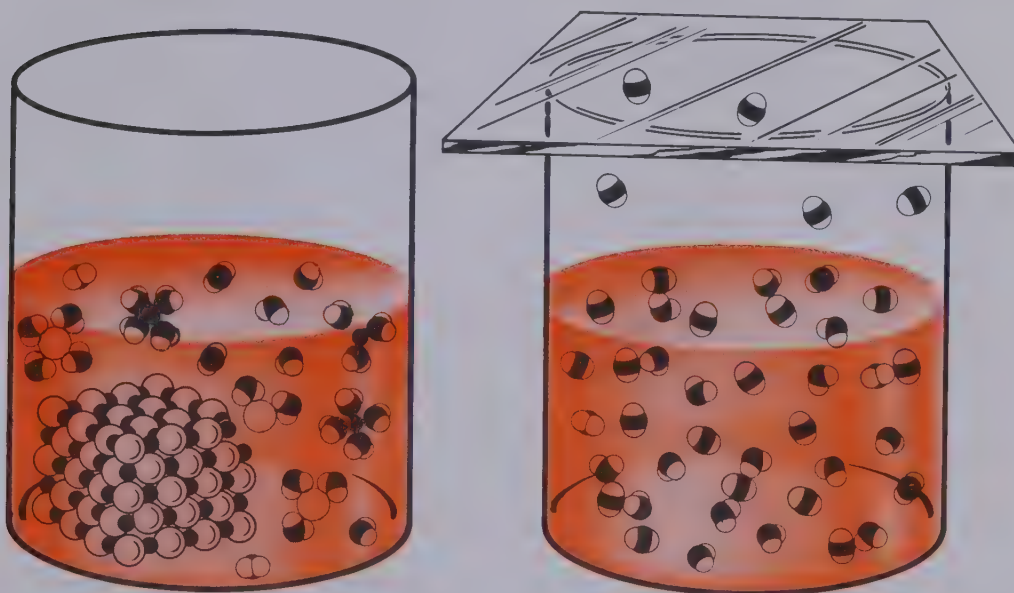
2. How many grams of cane sugar, $C_{12}H_{22}O_{11}$, would be needed to prepare 1 liter of a 0.2 molar solution?
3. How many grams of sodium iodide would be needed to prepare 25 cc of a 0.5 molar solution?
4. How many grams of lead nitrate, $Pb(NO_3)_2$, would be needed to prepare 25 cc of a 2.0 molar solution?

3-11 • RANDOMNESS AND SOLUTIONS

When a solid crystal dissolves in water, the particles become dispersed in the solvent; they achieve a disordered condition. However, the potential energy of the system is *increased* because of the work done in overcoming the forces which held the crystal together. Of course, the release of hydration energy then tends to make the system more stable by lowering the energy content somewhat.

The extent to which a given solid will dissolve in a given solvent depends upon many factors that are not easy to predict. The most reliable way to determine the solubility of a solid is to obtain experimental data in the laboratory. However, we will list a few generalizations.

1. For solids dissolving in liquids:
 - a. Tendency to randomness favors solution.
 - b. Hydration energy is an important factor. If much hydration energy is released, solution is favored; but if little hydration energy is released, the solid is not as likely to dissolve.
 - c. A high energy requirement to overcome crystal forces does not favor solution.



How does the randomness of a gas in solution in a liquid compare with that of a solid in solution in a liquid?

2. For gases dissolving in liquids:
 - a. Randomness favors the gas phase, *not* solution.
 - b. The tendency toward minimum energy favors solution, especially if a large amount of hydration energy is released.

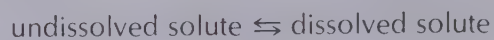


Dry Ice in water produces an interesting situation. Contrast the randomness of the carbon dioxide (1) as a solid, (2) in solution in the water, and (3) as a gas.

3-12. EQUILIBRIUM IN SOLUTIONS

When we deal with gaseous solutions, there is apparently no limit to solubility, for gases mix in all proportions. The same is true of certain liquid-liquid solutions. Water and alcohol, for example, can be dispersed, or dissolved, in all proportions. But when we consider liquid-solid solutions, there is a limit to the solubility of the solid.

In Exp. 3-5 you found that a fixed amount of crystals of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, dissolved in 3 cc of water at room temperature. The continued addition of crystals simply increased the amount of undissolved solid on the bottom of the test tube. We say the solution is saturated because no more solute can be dissolved at the existing temperature. This is an example of dynamic equilibrium. There is an equal rate of exchange between the dissolved salt and the crystals which are not in solution:



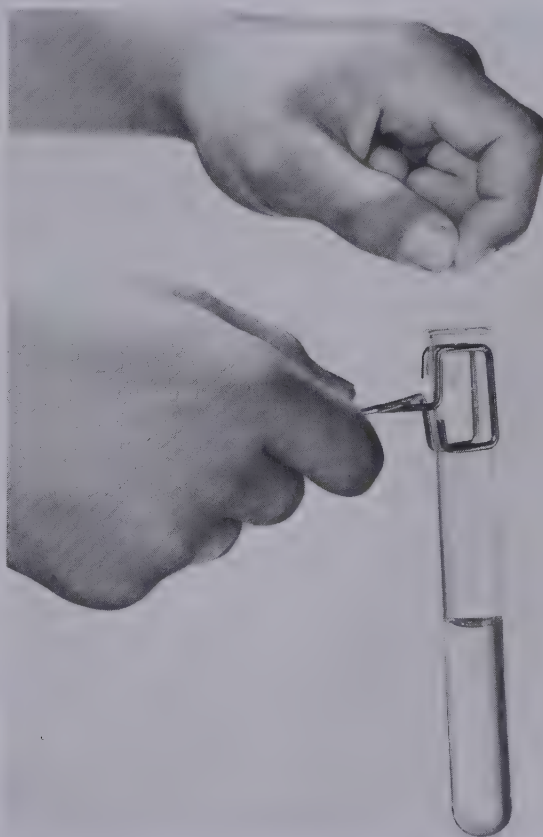
Although we cannot see this exchange, we can obtain laboratory evidence that it is happening. If a damaged crystal of sodium thiosulfate is placed in a saturated solution of sodium thiosulfate and the container is left undisturbed for a few days, the damage is repaired. We would also note that the weight of the crystal is unchanged; it is a bit smaller than before by an amount equal to the material required to fill up the damaged spot. Although we cannot see it happening, as some particles from this crystal dissolve, other particles in solution are deposited on the crystal, at an equal rate. The particles that are

deposited, however, tend to lodge on the damaged part, eventually filling it and restoring the crystal to its natural condition.

From facts like these we conclude that in a saturated solution there are two processes going on: the dissolved solid is recrystallizing at the same rate as the undissolved solid is going into solution. We define a *saturated solution* as one in which the solute in solution is in equilibrium with the undissolved solid.

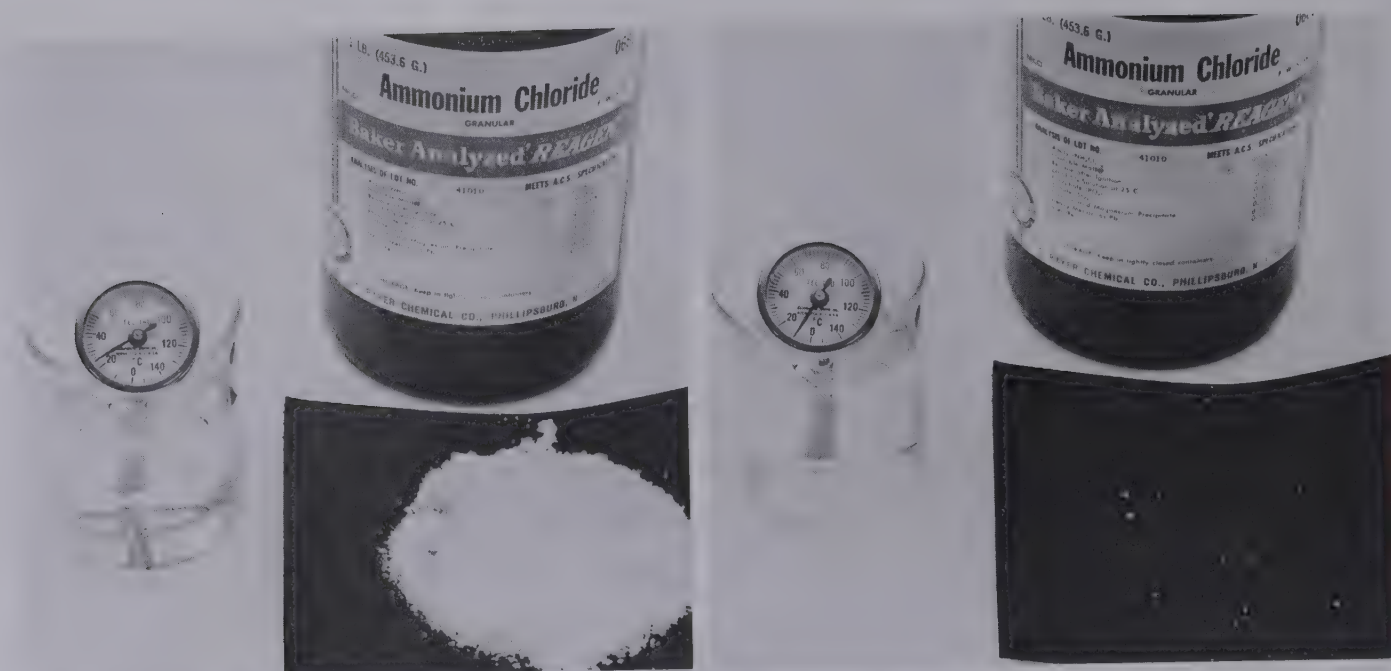
Supersaturated Solutions

Supersaturated solutions do not represent equilibrium, because there is no undissolved solid to dissolve. We define a *supersaturated solution* as one which contains more solute than it could normally dissolve at the existing temperature, or one containing more solute than it would at equilibrium conditions. In Exp. 3-5 you were able to dissolve 15 grams of sodium thiosulfate in 3 cc of water by gently heating the mixture until solution was complete.



What happens to the sodium thiosulfate solution when the crystal is dropped into it?

At this point you had a hot, almost saturated solution. Then upon careful cooling, all of that solute still remained in solution at room temperature. Evidence of the instability of such a solution was obtained by dropping a single crystal of solute into the mixture. Rapid crystallization occurred with the evolution of heat. Since heat energy was applied during the solution process, we would expect this same amount of heat to be released as crystallization occurs. This is in accordance with the Law of Conservation of Energy.



Is the dissolving of ammonium chloride in water an endothermic or exothermic reaction?

3-13. EFFECT OF TEMPERATURE ON SOLUBILITY

Raising the temperature tends to favor the more random state of a system. We can predict the effect of temperature on the solubility of a solid if we have some information about the solution process. According to Le Chatelier's Principle, if an equilibrium system is subjected to a stress, it will react in such a manner as to counteract the effect of the stress. Therefore, if a solid dissolves *endothermically*, increasing the temperature of the solvent increases the solubility. Since energy is absorbed in the process, the addition of heat will cause the system to react in a way that will use up the heat. As a result more solid will dissolve until a new equilibrium is established. Most solids dissolve endothermically, and so we expect increasing the temperature of the solvent to increase the amount of those solids in solution at equilibrium.

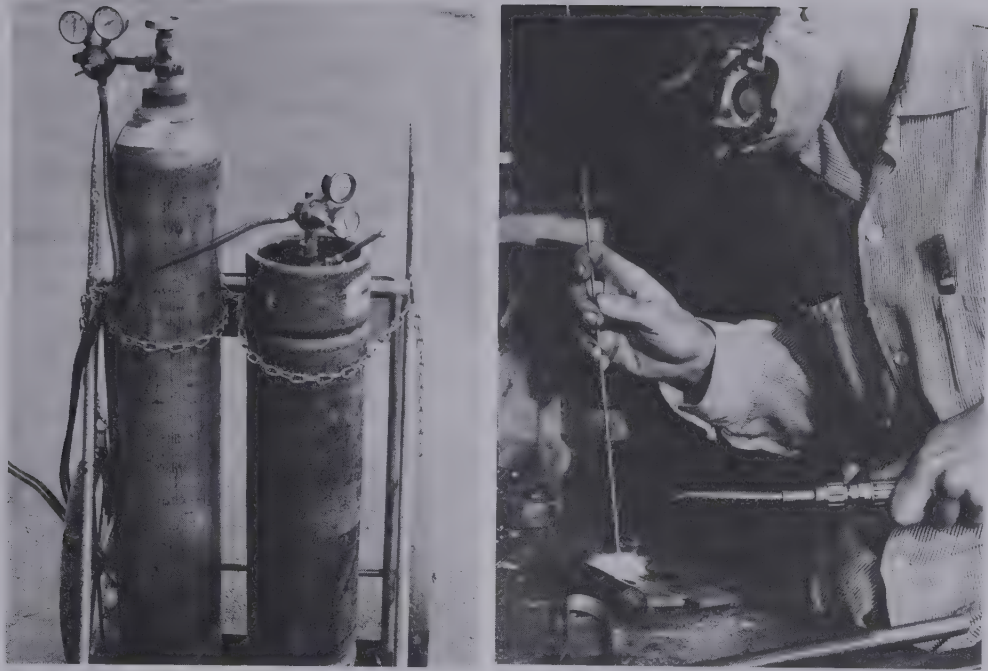
Some solids dissolve *exothermically*. For these, an increase in temperature decreases the amount of solute in solution at equilibrium. The system reacts to use up the added heat, and this favors crystallization.

Gases usually exhibit solubility trends which are opposite from those of solids. Since increasing the temperature of a system always favors randomness, we would expect to find in the laboratory that gases are *less* soluble in liquid as the temperature rises. You have seen dissolved air come out of water when the temperature is raised, and you know that carbon dioxide escapes from a warm carbonated beverage at a rapid rate. (There are some gases, however, which are more soluble at higher temperatures.)

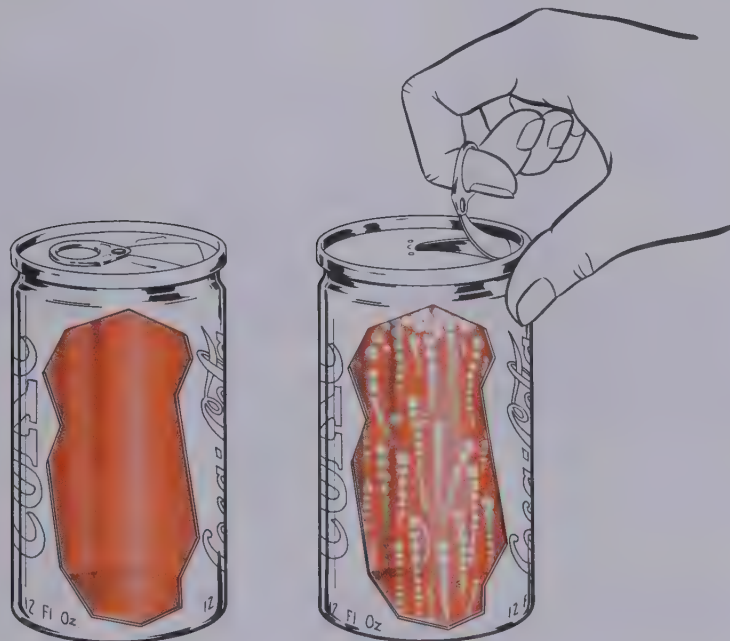
3-14. EFFECT OF PRESSURE ON SOLUBILITY

Solids and liquids are almost totally incompressible, and so pressure has little effect upon their solubility. Gases are compressible and are greatly affected

Acetylene gas for welding is dissolved in acetone under a pressure of sixteen atmospheres and stored in cylinders. The cylinders also contain a mixture of sandstone, charcoal, and asbestos that is 98% pore space.



by pressure. There is a direct relationship between pressure and the amount of a gas that can be dissolved in a given volume of liquid. In the production of carbonated beverages, carbon dioxide gas is dissolved in water under pressure up to ten times that of atmospheric pressure. When the can or bottle is opened the pressure on the liquid is reduced, and some of the dissolved carbon dioxide comes out of solution; we say that it "fizzes." It is dangerous to store carbonated beverages in a warm place because increasing the temperature tends to cause the carbon dioxide to come out of solution. If the pressure builds up sufficiently inside a very warm, capped bottle, the bottle might explode.



Does your experience with carbonated drinks support what is depicted here?

3-15 • SOLUTIONS AND ELECTRICITY

By the end of the eighteenth century scientists were searching for an explanation for the behavior of solutions. They knew that certain solutions, such as sodium chloride in water, conducted an electric current, while a sugar solution did not. They were puzzled about why distilled water did not conduct a current, whereas tap water did. It remained for Michael Faraday to answer these questions.

Faraday was born in 1791 in London to very poor parents. He had little schooling and at the age of thirteen began to work for a bookbinder. He developed an interest in science and read all books available to him. In 1810 Faraday attended a series of lectures given by Sir Humphrey Davy, a famous scientist. Faraday took full notes of the lectures and bound the notes into a book. (He worked for a bookbinder, you remember.) Shortly afterwards he wrote a letter to Sir Humphrey Davy asking for employment in his laboratory. He also sent his neatly written, bound notebook. Faraday's ability to record well what he had heard induced Davy to hire him. Later, Davy said that Faraday was the greatest of all his discoveries.

Many years later, in 1833, Faraday published the report of his extensive research on the electrical conductivity of solutions. He believed that conducting solutions contained particles which were able to carry the current from one place to another. He called these particles *ions*, and he called solutions of ions *electrolyte* solutions. He was the first to use the term electrolyte to describe solutions which are able to conduct an electric current.



The needle on the meter has swung completely off scale, indicating that the solution of copper nitrate in the beaker is an excellent conductor.

The Swedish chemist, Svante Arrhenius (1850–1927), later published a work on the properties of electrolytes, which he had also studied in his laboratory. He thought that when molecules ionized in water, they produced both positive and negative ions. He believed that ionization is complete only in very dilute solutions and that in concentrated solutions the ions are in equilibrium with non-ionized molecules. These ideas, known as the Theory of Ionization, have guided chemists in their study of solutions to the present time. It is only recently that knowledge of crystalline structure has caused the modification of some of the concepts proposed by Arrhenius. We will explore the ability of solutions to conduct a current in Chapter 4.

Suggestions for Creative Work

1. Obtain an uncalibrated thermometer and devise a method for calibrating it.
2. Devise a method for checking the accuracy of a thermometer used in the laboratory.
3. Plan and perform an experiment for determining the heat of fusion for water.
4. Plan and perform an experiment for determining the heat of vaporization for water at its boiling temperature.
5. Apply the principles of vaporization and condensation of liquids to explain how a refrigerator works. Can you cool a room effectively by leaving the refrigerator door open? Give reasons for your answer.
6. How does the wet-bulb thermometer demonstrate that evaporation is a cooling process?
7. Apply your knowledge of solutions to explain the formation of:
 - a. Stalagmites and stalactites in caverns.
 - b. Carlsbad Caverns.
 - c. Mammoth Hot Springs in Yellowstone National Park.
 - d. Fossil records from the past.
 - e. Natural pearls by oysters.
8. Research what happens to the water in a lake between fall and the following summer.

Suggestions for Creative Writing

1. Investigate possible sources of water pollution in your community and write an article designed to arouse the public to take corrective measures. Apply your knowledge of scientific procedures and remain objective.
2. Write a paper explaining some of the properties of water and/or the effect of water on climate that would be meaningful to a grade school youngster. Choose any age or grade level and write accordingly.

Practice Exercises *(Answers on pp. 310, 311)*

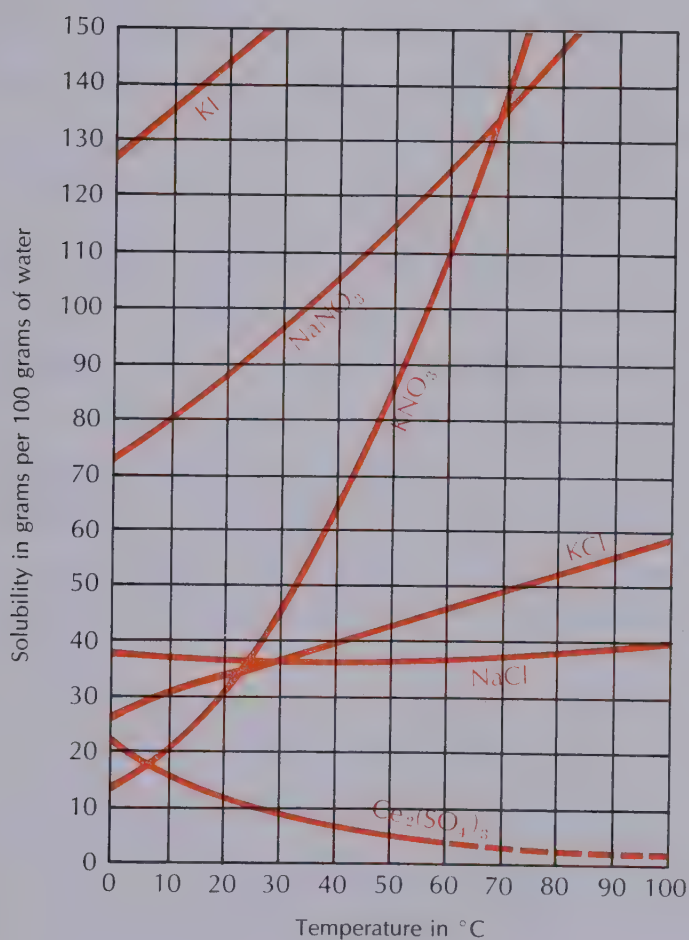
1. Illustrate by means of a drawing how the intermolecular spaces differ in liquids, solids, and gases.

2. Explain why liquids diffuse very slowly.
3. Which will evaporate faster, a beaker of water at room temperature or one in which the water has been heated to 50° C? Give reasons for your answer.
4. What three conditions are necessary in order to have an equilibrium system?
5. Explain why evaporation is a cooling process.
6. Which of the following represent equilibrium systems and which are steady state?
 - a. A well-fed canary (in a cage) whose weight is constant.
 - b. A sugar solution in a covered beaker with sugar crystals visible in the bottom of the beaker.
 - c. A bottle of vinegar on a supermarket shelf.
 - d. A classroom in which there are 24 students each period.
7. Attempt to arrange the following liquids in order of decreasing vapor pressure based on the boiling temperatures which are given after each liquid. Assume all of the substances are at room temperature.
 - a. methanol—64.7° C
 - b. carbon tetrachloride—76.7° C
 - c. ethyl chloride—12.3° C
 - d. phenol—181.9° C
8. Recall the ammonia water-water equilibrium system you observed in Exp. 3-1. Predict the effect of the following changes on the equilibrium system:
 - a. Reducing the size of the covering beaker.
 - b. Increasing the size of the covering beaker.
 - c. Increasing the temperature of the system.
 - d. Adding more ammonia water.
9. What is meant by the words "equilibrium vapor pressure"?
10. Name four general properties common to all solutions.
11. Why does the tendency toward maximum randomness favor the solubility of solids in liquids, but not of gases in liquids?
12. Describe the structure of the water molecule and explain why it is said to be polar.
13. List five physical properties of water. List four chemical properties of water.
14. Define: ion, solution, solute, solvent, boiling point, diffusion.
15. Calcium metal reacts with water to form what products?
16. List three common actions of daily living that are promoted by the presence of water.
17. Why is the climate more uniform on the seacoast than on the prairies?
18. Why does the density of water decrease when heated above 4° C and also when cooled below that temperature?
19. How many grams of solute would you need to make the following solutions?
 - a. 1 liter of 1-M $\text{Ca}(\text{NO}_3)_2$

- b. 500 cc of 1-M KOH
- c. 250 cc of 0.5-M Na_2SO_4
- d. 100 cc of 6-M $\text{HC}_2\text{H}_3\text{O}_2$

Self-Test (Answers on pp. 311, 312)

1. Water has its maximum density at what temperature? (a) 0°C (b) 32°F (c) 100°C (d) 4°C
2. During the process of vaporization at a given temperature, particles leaving a liquid undergo which of these changes? (a) loss of potential energy (b) gain of potential energy (c) loss of kinetic energy (d) gain of kinetic energy
3. How many grams of NaNO_3 would you use to prepare 250 cc of a 0.2-M solution?
4. Refer to the graph and answer the following questions:
 - a. Give a formula for a substance which dissolves exothermically.
 - b. A solution of KCl in 100 g of water is saturated at 10°C . How much additional KCl must be added to saturate the solution at 80°C ?
 - c. How many grams of NaCl are in a saturated solution at 100°C ?



5. List the following liquids in order of *increasing* boiling temperatures, basing your predictions on the vapor pressures at 0°C , which are listed after each liquid.
 - a. ethanol—43.9 torr
 - b. acetic acid—11.7 torr
 - c. carbon disulfide—298.0 torr
 - d. benzene—77.0 torr
 - e. diethyl ether—442.2 torr
6. A solution in which the dissolved solute and the undissolved solute are in equilibrium is said to be (a) saturated, (b) unsaturated, (c) supersaturated, (d) impossible.
7. A gas-liquid system is observed to be in equilibrium. Apply Le Chatelier's Principle to predict the effect of the following changes. State in each case whether the gas or the liquid phase will be favored.
 - a. Raising the temperature. \rightarrow decrease solubility
 - b. Increasing the pressure. \rightarrow increase solubility
 - c. Increasing the volume of the container.
8. Why does steam at 100°C contain more potential energy than water at 100°C ?
9. In which of the following climates would you expect the seasonal turn-over in large lakes to be more noticeable: climate A, where the average summer temperature is around 65°F , or climate B, where the average summer temperature is around 100°F ? Give a reason for your choice.
10. Sketch a model of a water molecule and explain why it is polar.
11. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION

Steam at 100°C produces a more severe burn than water at 100°C .

REASON

Because steam at 100°C contains more potential energy than an equal amount of water at 100°C .

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INGREDIENTS: Concentrated non-fat milk; sucrose; partially hydrogenated vegetable fat; dutch-processed cocoa; sodium caseinate; carrageenan; vanilla and artificial vanilla; ascorbic acid; ferrous sulfate; niacinamide; alpha tocopherol; zinc sulfate; copper gluconate; manganese sulfate; calcium pantothenate; thiamine hydrochloride; Vitamin A palmitate; calciferol; pyridoxine hydrochloride; riboflavin; cobalamin.

NO CYCLAMATES
NO SACCHARIN





ACIDS, BASES, AND SALTS

OBJECTIVES:

By the time you have completed your study of Chapter 4, you will be expected to demonstrate acceptable performance on the following objectives.

1. State the accepted definition for:
 - a. electrolyte
 - b. nonelectrolyte
 - c. acid
 - d. base
 - e. salt
 - f. neutralization
 - g. hydrolysis
 - h. buffer
 - i. chemical indicator
 - j. common ion effect
2. State the assumptions in the Arrhenius Theory of Ionization and *discuss* the present day theory of acids and bases.
3. *Apply* your knowledge of the general properties of acids and bases and *identify* a sample of liquid as an acid or a base by conducting appropriate laboratory tests.
4. State the name of an acid, base, or salt, given its formula.
5. *Explain* why NH_3 is a better base than H_2O by comparing the properties of these two compounds.
6. *Predict* the pH of a salt solution qualitatively, given its formula.
7. *Apply* Le Chatelier's Principle to explain the common ion effect when sodium acetate is added to a solution of acetic acid.
8. Write an ionic equation to illustrate the hydrolysis of a salt.
9. State the pH of a solution, given the molar concentration of the H_3O^+ ion.
10. *Determine* the pH of a solution by the most precise method available to you.
11. *Explain* why sulfuric acid, H_2SO_4 , is a strong electrolyte and why acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is a weak electrolyte.
12. Explain why carbon tetrachloride, CCl_4 , is a nonelectrolyte.

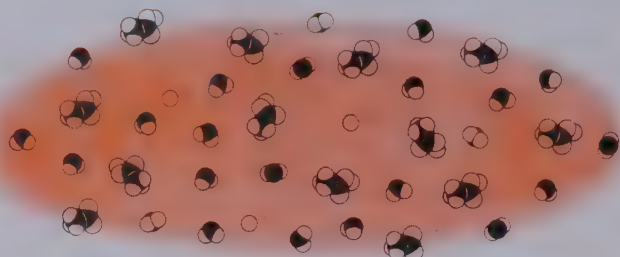
SUGGESTED ORDER OF STUDY

1. Observe Demonstration Exp. 4-1. Record data in laboratory record book and hand in formal report.
2. Study Secs. 4-1 through 4-4.
3. Perform Exp. 4-2. Hand in formal report.
4. Study Secs. 4-5 through 4-13.
5. Perform Exp. 4-3. Hand in formal report.
6. Study Secs. 4-14 and 4-15.
7. Perform Exp. 4-4. Hand in formal report.
8. Study Sec. 4-16.
9. Review and do supplementary reading.
10. Do the Practice Exercises and review as needed.
11. Take the Self-Test and review as needed.
12. Take Chapter 4 test.

4-1. IONIZATION THEORY

Michael Faraday was one of the first scientists to work in the field of electrochemistry. The experiments he performed were much like your investigations in Exp. 4-1. Faraday attempted to explain his observations by assuming that

atoms are electrical in character. About 50 years later, in 1887, Svante Arrhenius formulated a theory of ionization to account for the chemical properties of acids, bases, and salts. Since the time of Faraday and Arrhenius new instruments and improved techniques have led to the modification of their ideas. However, these two men laid the foundation for electrochemistry. Let us examine the details.



An artist's depiction of a solution of acetic acid in water according to Arrhenius' theory.

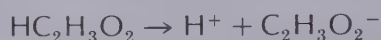
In Exp. 4-1 you found that solutions of hydrogen chloride, sodium hydroxide, and sodium chloride conduct current very well. Substances such as benzene, alcohol, and carbon tetrachloride do not conduct current. As we indicated at the end of Chapter 3, Faraday knew this from his observations, too, and suggested the name *electrolyte* for substances in solution that permit a current to flow and the name *nonelectrolyte* for those substances that do not conduct a current. Arrhenius considered the questions: What makes an electrolyte a conductor of current in a solution? Why doesn't a nonelectrolyte conduct a current in solution? He tried to answer these questions by his theory of ionization, which can be summarized as follows:

1. Molecules of electrolytes break apart in water solution to form electrically charged particles called ions.
2. Both positive and negative ions are formed by this dissociation.
3. The total number of positive charges is equal to the total number of negative charges in the solution; that is, the solution itself is electrically neutral.
4. The molecules and ions in solution are in equilibrium with each other.
- ⑤ The extent of ionization depends upon the amount of water present; the addition of water favors the formation of ions.
6. Nonelectrolytes remain as molecules in water and do not form ions.

4-2· WEAK ELECTROLYTES

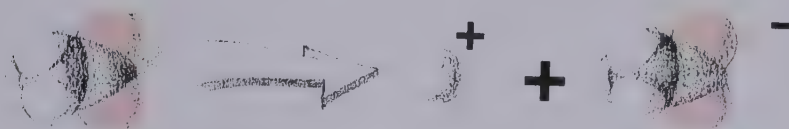
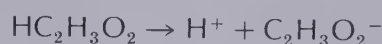
We can apply the theory of Arrhenius to the observations we made in Exp. 4-1 with acetic acid. According to this theory, molecules of acetic acid separate to form positive and negative ions in solution. This can be expressed in two ways, in English and in a chemical equation:

Acetic acid molecules form ions in solution



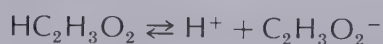
Both statements convey the basic information, but the chemical equation gives more. For example, it tells us which ions are formed in solution, according to Arrhenius' theory. It states that positively charged hydrogen ions, H^+ , and negatively charged acetate ions, $C_2H_3O_2^-$, are formed from acetic acid molecules, $HC_2H_3O_2$. The arrow can be translated into a number of English words: form, make, produce, or yield.

Scientists like to use equations because they convey a great deal of information in little space. The first three parts of the theory summarized in Sec. 4-1, three sentences, are all expressed by this equation:



1. The equation shows the formation of ions from molecules.
2. The equation shows both positive and negative ions.
3. The equation shows as many positive as negative charges.

To include a fourth statement, one about equilibrium, an arrow pointing in the other direction must be added:



This equation now tells us that the ions will form molecules. Both arrows are the same length, which can signify for us that the rate at which molecules form ions is the same as the rate at which ions form molecules again. So, according to Arrhenius' theory, a solution of acetic acid, which looks as though nothing much is happening in its bottle in the laboratory, actually is a very busy place. Molecules are forming ions and ions are forming molecules.

In Exp. 4-1 you found that solutions of acetic acid did not conduct very well. From this, we can guess that there were not very many ions present in the solution; most of the acetic acid must be in the form of molecules with only a small part of it in ionized form. Today, we have modified Arrhenius' theory to explain how this might be possible.

Definition of an acid and a base

Acetic acid is an acid. That is, hydrogen ions can be taken from it. Some chemists prefer to say that *an acid is a proton giver or donor. Proton is another word for hydrogen ion, H^+ .* However, acetic acid is stingy with its protons; it gives them away reluctantly.

A base is a proton taker. A good base takes protons vigorously. A poor base takes protons, just as a good base does, but a poor base takes protons more or less as though it didn't really care very much. Water is a medium kind of base, not really poor, but not very good, either. Here is an equation:

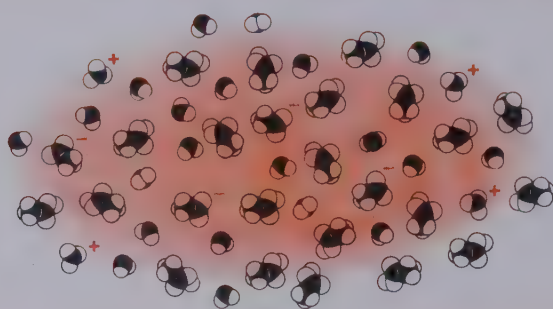


This equation says that acetic acid molecules react with water molecules to form (or produce) hydronium ions and acetate ions. The plus sign on the left stands for "reacts with," and the plus sign between the two formulas on the right stands for "and." As you have guessed, H_2O is the formula for water; the formula for hydronium ions is H_3O^+ . As the formulas show, a hydronium ion is a water molecule that has taken a proton.

What about the arrow pointing the other way? How do we get it into the equation? To do this, you must know that the acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, is a good base. It would take a proton from its own grandmother and not be sorry. Hydronium ions have protons; so, about as fast as an acetate ion manages to sneak up on a hydronium ion, it snatches a proton away. When a proton leaves a hydronium ion, water remains; when an acetate ion gets a proton, it becomes an acetic acid molecule. Here is the complete equation:



The arrow pointing to the left is shown as a thicker arrow to indicate the stronger tendency. The two ions tend to react more than the two molecules. Both arrows are the same length to indicate that the rates of the two reactions are equal.

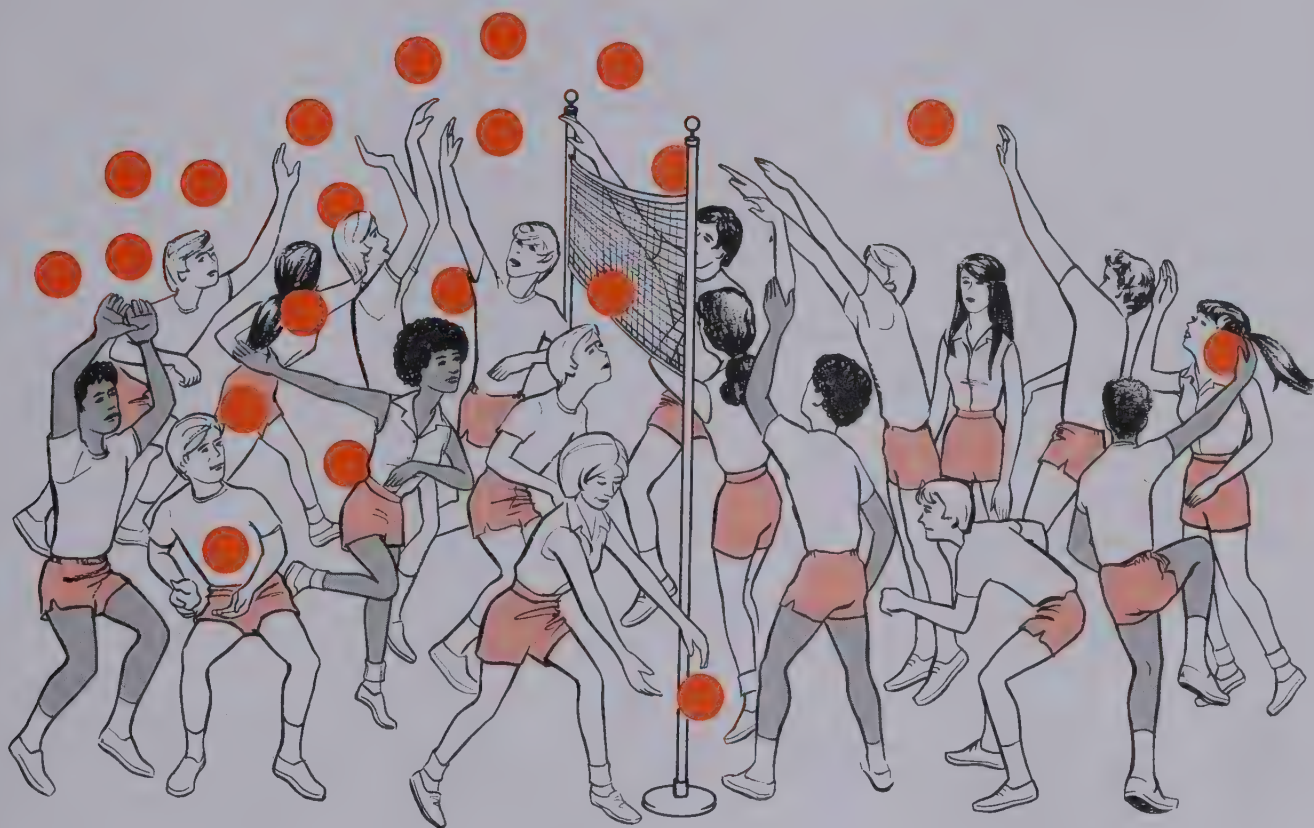


Unequal vigor, equal rates

Many students who have learned what you have just learned have wondered how the opposite rates can be equal when the vigor of the opposite reactions is so different. Offhand, you would think that if the ions reacted vigorously,

the rate from right to left would be fast. And you would think that if the molecules reacted like they didn't care much if they did or not, the rate from left to right would be slow. This is correct. But it is not the whole story.

To understand this, it will help if we make a model in our imagination. One helpful model is a new kind of volleyball game. The game is the same as the regular game except that there are maybe twenty balls used instead of only one. So, to start with our imaginary model, think of a volleyball game with pretty good players getting the balls back and forth across the net. At any one time, there would be a lot of balls in the air. Kind of exciting to think about! Or maybe silly.



Anyway, now imagine that both teams are good, but one team is slow in getting the ball back across the net; they keep it on their side for quite a while before it finally gets knocked across the net. The other team is fast in their ball handling. Just about as soon as any ball comes over to them, back it goes to the slow ball handlers. So, in this game, at any one time, most of the balls are on the slow team's side of the net. Every once in a while though, they get the ball over to the fast side. Then, bang! back it goes to their side. The rate at which balls go from the slow to the fast side, on the average, is equal to the rate at which balls go back the other way. The fast team can knock the balls back only as fast as they come over, which isn't very fast. So the two rates, balls going over one way and back again, are slow. But both rates are equal. Most of the balls at any one time are on the slow side. Only a few balls are ever on the fast side at any one time.

This is how we can have equal rates even when one side is fast and the other slow. Applied to the acetic acid solution, it means that at any one time, very few ions exist, compared to the number of molecules.

Dynamic Equilibrium

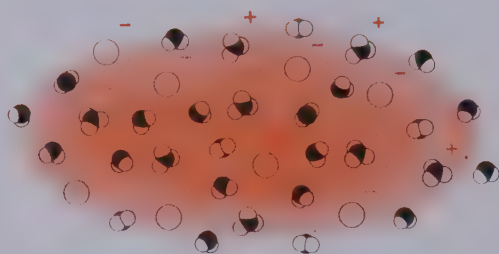
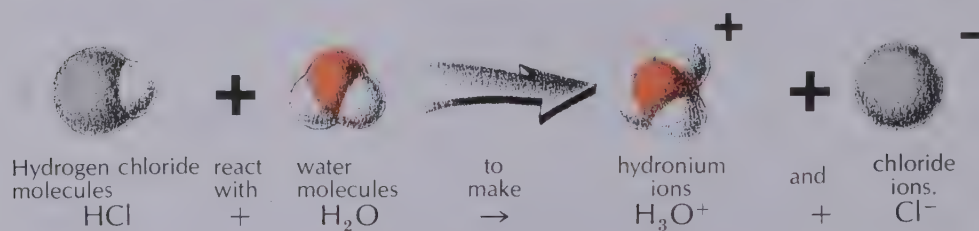
When two rates are equal and opposite, scientists say that the system is in dynamic equilibrium. The system could be the imaginary volleyball game or it could be the acetic acid solution.

Acetic acid in a water solution is called a *weak electrolyte* because there are not many ions compared to the number of molecules. Acetic acid is a weak electrolyte because it is a poor acid compared to how good a base the acetate ion is. The acetate ion is vigorous in taking protons from hydronium ions, and the acetic acid is not much interested in giving up a proton. So, when the system is in dynamic equilibrium, there are only a few ions and many molecules.

We can now explain the laboratory observation that a weak electrolyte is a substance in solution which does not conduct a current very well. It is a poor conductor because there are only a few ions and many molecules in the solution, according to our model. So, theoretically, in the laboratory or anyplace else, a weak electrolyte is a substance in solution which has few ions compared to the number of molecules.

4-3. STRONG ELECTROLYTES

You can almost guess from the name that a *strong electrolyte* is a substance which has many ions. This is correct, but there is a little more. A strong electrolyte has no molecules at all. It is all in the form of ions. A water solution of hydrogen chloride (commonly known as hydrochloric acid) is a good example of a strong electrolyte. Here are the English sentence and the chemical equation.



In this example we should first notice the strong acid, hydrogen chloride. It is called a strong acid because it ionizes completely in water solution. We can think of it as a good acid, also, because it is very generous with its proton. Hydrogen chloride practically forces any base to take its proton. Next, notice the chloride ion. Of all the bases, the chloride ion is about the poorest. The chloride ion will hardly take a proton from anything. It certainly will not take a proton from a hydronium ion, even though the hydronium ion is a very good acid and will give its proton away almost with no complaints. The result, of course, is that we cannot correctly put an arrow pointing the other way in our chemical equation.

In the laboratory a strong electrolyte is a substance in solution which conducts a current very well. According to the theory, or model, it conducts well because all of it is in the form of ions, with no molecules.

Ion Pairs

Actually, we should hedge a little bit. According to the theory, chloride ions and hydronium ions are oppositely charged, so they do attract each other. In solution every once in a while, or maybe lots of times, one of the chloride ions happens to pass near a hydronium ion. When this happens, they do hang around each other for a little bit before they go off alone again. So, at any one time, you could find some ion pairs, a hydronium ion and a chloride ion, here and there. But they would soon separate without any shifting of the proton from the hydronium ion to the chloride ion; there would be only an ion pair.

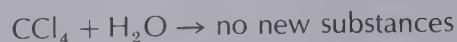


The interaction of ions of opposite charge in a solution.

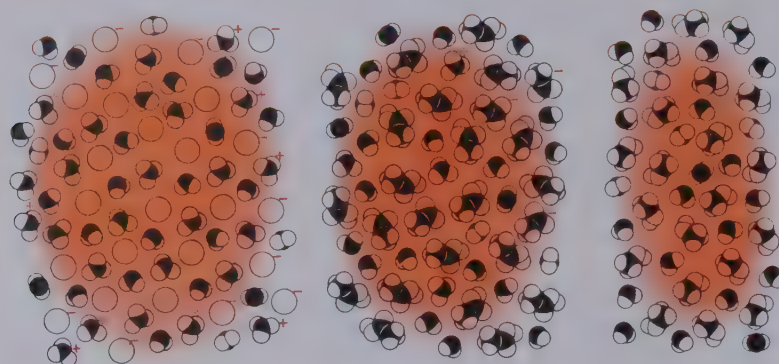
4-4. NONELECTROLYTES

In the laboratory a nonelectrolyte is defined by its behavior: it does not conduct a current at all. According to our theory, a nonelectrolyte is defined as a substance which does not form ions in solution; all of it stays as molecules.

Here is a chemical equation to express this idea:



This equation indicates that carbon tetrachloride does not react with water. Other examples of nonelectrolytes include benzene, alcohol, sugar, gasoline, and glycerine.



A strong electrolyte (left), a weak electrolyte (center), and a nonelectrolyte (right).

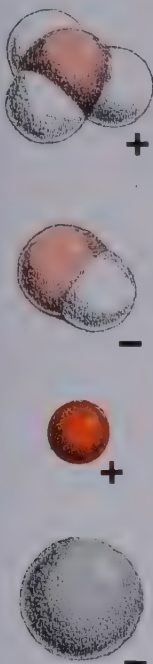
We can summarize our discussion of electrolytes and nonelectrolytes by comparing strong and weak electrolytes and nonelectrolytes. In solution a strong electrolyte is all ions, with some ion pairs. A nonelectrolyte is almost the exact opposite: no ions, all molecules. A weak electrolyte is in between: a few ions and many molecules. Remember, there is no known example of the other kind of electrolyte you may have wondered about—one with a lot of ions and a few molecules.

4-5. PROPERTIES OF ACIDS

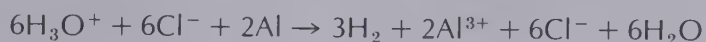
Compounds whose water solutions contain ions are classified as acids, bases, or salts. An acid is a compound which will give up or donate a proton (a hydrogen ion, H^+). Strong acids will do so completely; weak acids do so incompletely and remain mostly as molecules because of the dynamic equilibrium we have discussed. Hundreds of acids are known; most of them are weak acids. Nearly all fruits contain acids. The citrus fruits, lemons, oranges, and grapefruit, contain a weak acid called citric acid. Vinegar contains acetic acid, and this acid is weak, as we know. Aspirin is acetylsalicylic acid, another weak acid.

When an acid is dissolved in water, hydronium ions are formed. This applies to both strong and weak acids. The presence of the hydronium ion, H_3O^+ , is responsible for the properties we associate with acids.

1. *Acids taste sour.* Lemons, oranges, and grapefruit taste sour because they contain weak acids in water solution. Most acids used in the laboratory are poisons and extremely corrosive to flesh, so *never* use the "taste test" to identify substances unless you are instructed to do so.

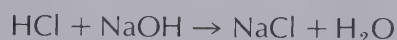


2. *Acids in solution affect indicators.* Litmus paper contains a dye which turns red in the presence of hydronium ions. Other indicators may be used to detect an acid, as you will find when you perform experiments with acids in the laboratory.
3. *Acids react with many metals.* You found in an early experiment that hydrochloric acid reacts with aluminum to produce hydrogen gas and the salt, aluminum chloride:

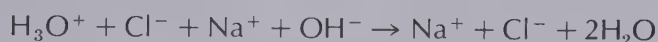


This chemical equation says that hydronium ions, chloride ions, and aluminum metal react to yield hydrogen molecules, aluminum ions, chloride ions, and water. The numbers on the left of the symbols tell us how much of each substance is involved; we will discuss this in more detail later.

4. *Acids neutralize bases, often forming a salt and water.* When an acid and a base are mixed in proper quantities, water and a salt are often produced. Let us represent this reaction by showing the equation for the reaction between hydrochloric acid, HCl, and sodium hydroxide, NaOH, a base:



Written to show the presence of ions:

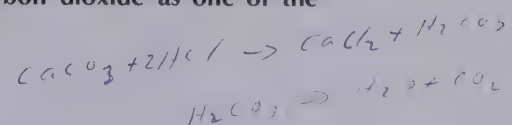


Notice that the positive ion in the salt comes from the parent base and the negative ion in the salt comes from the parent acid.

5. *Acids react with carbonates.* When the hydronium ion of an acid reacts with a carbonate, the products are a salt, carbon dioxide gas, and water. Sour milk contains lactic acid, a weak acid. Baking soda is a carbonate, sodium hydrogen carbonate. So, sour milk will react with baking soda to produce carbon dioxide gas. The gas forms small bubbles in biscuit dough and makes it rise. The other products formed need not concern us since it is against the rules to make biscuits while reading a chemistry book.



An acid reacts with limestone, CaCO_3 , to produce carbon dioxide as one of the products.

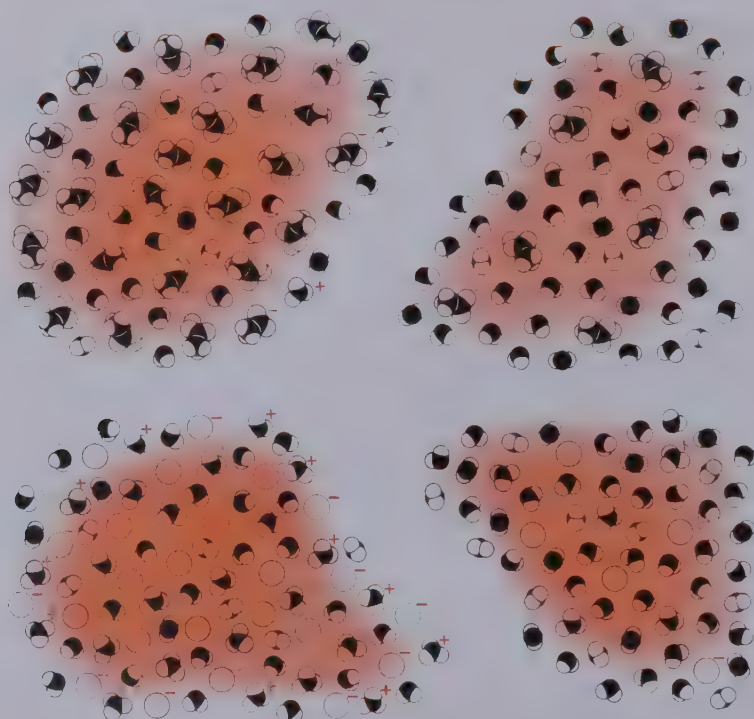


4-6 • STRONG AND WEAK ACIDS

An acid that is a strong electrolyte is called a strong acid; one which is a weak electrolyte is called a weak acid. It is important to remember that the strength and the concentration of an acid are different. When we speak of the *strength* of an acid, we are referring to the *relative number of hydronium ions it forms in solution*. Strong acids furnish large numbers of hydronium ions and are good electrolytes. Examples are hydrochloric acid, HCl ; sulfuric acid, H_2SO_4 ; and nitric acid, HNO_3 . Weak acids furnish relatively few ions in water solution and are poor electrolytes. Examples are acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, and carbonic acid, H_2CO_3 . Carbonic acid is the weak acid found in soft drinks.

The *concentration* of an acid refers to the *total amount of it that is dissolved in water*. If a large amount of acid is dissolved in each liter of water, we say that the solution is *concentrated*. If very little is dissolved in each liter of water, we say that the solution is *dilute*. If a medium amount is dissolved, we might say either concentrated or dilute, depending upon how we felt at the moment. Concentrated and dilute are qualitative expressions of concentration, that is, how much is dissolved.

A solution of a weak acid can be either dilute or concentrated. In either kind of solution the comparative number of ions is small in relation to the number of molecules. A solution of a strong acid can be either dilute or concentrated. In either kind of solution all of the acid would be ionized, but a dilute solution would contain fewer ions than a concentrated solution.



Identify which of these four representations are for (1) a concentrated strong acid, (2) a dilute strong acid, (3) a concentrated weak acid, and (4) a dilute weak acid.

4-7. NAMING ACIDS

Acids that contain only two elements are known as *binary* compounds. They contain hydrogen as the positive part. Binary acids contain one nonmetallic negative part in addition to the hydrogen. The name of the binary acid begins with the prefix *hydro-* and ends with the suffix *-ic*. The stem of the name of the nonmetallic element makes up the central part of the name (Table 4-1).















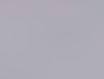
Names and Formulas of the Common Acids			
	Name of Acid		Formula
	Binary:	hydrochloric	HCl
		hydrobromic	HBr
		hydrosulfuric	H ₂ S
	Oxyacids:	sulfuric	H ₂ SO ₄
		sulfurous	H ₂ SO ₃
		nitric	HNO ₃
		nitrous	HNO ₂
		perchloric	HClO ₄
		chloric	HClO ₃
		chlorous	HClO ₂
		hypochlorous	HClO
		acetic	HC ₂ H ₃ O ₂
		carbonic	H ₂ CO ₃
		phosphoric	H ₃ PO ₄
		phosphorous	H ₃ PO ₃

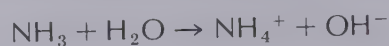
Table 4-1

Acids which contain oxygen in addition to a second nonmetal are known as *oxyacids*. The names of many of these acids end with the suffix *-ic* or *-ous*, depending upon the number of oxygen atoms present. Rather than to list the rules here, it is more useful to look at the names and formulas for some of the common acids. A complete list of rules for naming compounds is given in Appendix 4 for your reference.

4-8. PROPERTIES OF BASES

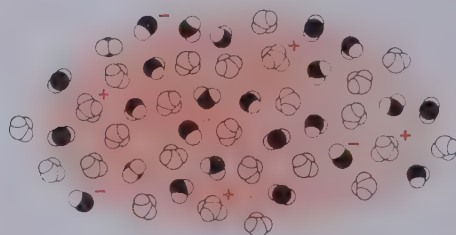
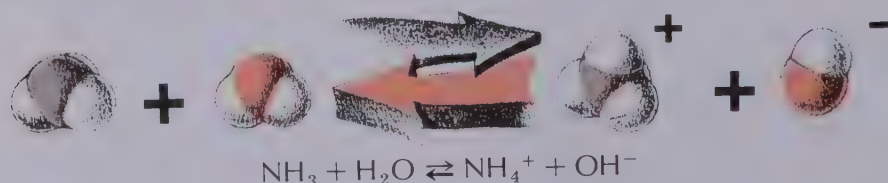
Almost every household uses a number of bases. Ammonia water is used for cleaning; lye is a commercial grade of potassium hydroxide; milk of magnesia, which is magnesium hydroxide, is used as a mild laxative; baking soda, which is sodium bicarbonate, is used in the kitchen.

We will use ammonia water as our first example. Ammonia, NH_3 , is a gas; it dissolves readily in water. The resulting solution is called ammonia water. (Years ago, the solution was called ammonium hydroxide, NH_4OH ; but today we know that this is incorrect. You may see the formula NH_4OH , however, on the bottles of ammonia water in your laboratory.) When ammonia is dissolved in water, it behaves as a fairly good base, not as good as some others, but good enough to take a proton from water. Here is the chemical equation:



This equation says that ammonia molecules react with water molecules to yield ammonium ions, NH_4^+ , and hydroxide ions, OH^- . But it is also important to read it this way: Ammonia is a base, and it takes a proton from water to form ammonium ions and hydroxide ions. This way of saying it emphasizes that ammonia is a base.

However, ammonia water is a poor conductor. There is a dynamic equilibrium involved in this system similar to that for the weak electrolyte solution of acetic acid. The ammonium ion is an acid, and the hydroxide ion is one of the best bases known. So, about as soon as ammonium ions and hydroxide ions are formed, the reaction in the opposite direction occurs. In dynamic equilibrium there are few ions compared to the number of molecules. Here is the complete equation:



According to the old Arrhenius theory of acids and bases, only hydroxide ions were thought of as bases. Today, we also think of other bases, such as the ammonia molecule, NH_3 , or the acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, as well as the hydroxide ion, OH^- .

In a water solution, any base will form hydroxide ions either from itself, as some strong bases do (this is discussed in Sec. 4-9), or by taking protons from water and forming hydroxide ions as one of the products; this is what ammonia does. So, in thinking about solutions of bases, it is helpful to think about solutions of hydroxide ions. Such solutions have these properties:

1. *Bases taste bitter.* We do not taste substances in the laboratory, but if you have ever taken milk of magnesia, you are aware of the bitter taste of bases. The main ingredient in milk of magnesia is magnesium hydroxide, $\text{Mg}(\text{OH})_2$.
2. *Bases cause a slippery feel.* The hydroxide ion in a solution of base reacts with some of the fatty tissue just under the layer of skin and converts that fat into soap, which then causes a slippery sensation. Care should be exercised when handling bases in the laboratory; you won't make much soap but you will lose a significant amount of protective fat, and your fingers will become very tender until your body has replaced the fat that was lost.
3. *Bases turn litmus blue.* The presence of the OH^- ion in bases causes litmus paper to turn blue. Other indicators may also be used to identify bases. One of the indicators frequently used in the laboratory is phenolphthalein. This is a white powder which we dissolve in alcohol to produce a colorless solution. In the presence of a medium concentration of OH^- ions, phenolphthalein turns pink. It is colorless in acid solutions, and it is colorless in solutions with a high concentration of OH^- ions.
4. *Hydroxide ions in solution react with hydronium ions to form water.* That is, acids and bases react and neutralize each other. This is a result of the H_3O^+ ion from the acid reacting with the OH^- ion to form water.

4-9. STRONG AND WEAK BASES

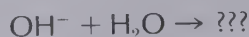
Like acids, bases can be classified as weak or strong. In a solution of a weak base there are many, many more molecules than there are ions. Ammonia water is an example. In a solution of a strong base, there are no molecules, only ions, as you can guess from what you have learned about other strong and weak electrolytes.

A good example of a strong base is sodium hydroxide. In water solution this compound ionizes completely, as expressed in this chemical equation:

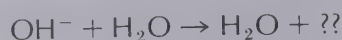


Since hydroxide ion is a strong base, you might think for a minute (before we add more information) that there would be an opposite reaction, just as there was when ammonia dissolved. But in this case the sodium ion, Na^+ , has no hydrogen ions, no protons, to be taken. So, there is no reaction in the other direction. In water solution sodium hydroxide is completely ionized. It is a strong base because the solution is completely ionized, thus providing large numbers of hydroxide ions.

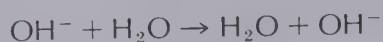
In a water solution there is some water which can act as an acid toward the hydroxide ions, giving them a proton:



What do you think the products might be? If the hydroxide ion takes a proton from anything, it becomes a water molecule:



And, if a water molecule loses a proton to anything, it becomes a hydroxide ion:



The net result is nothing new. Of course, it is a *different* hydroxide ion and a different water molecule now. But one is the same as the other, more like each other than identical twins; so, there is no net chemical change, none at all. It is quite correct to write the other arrow, to show that there is a dynamic equilibrium, but the net result is that there is no chemical change:



Calcium hydroxide is another strong base; it ionizes completely in water solution:



It happens, however, that not very much calcium hydroxide will dissolve in water; the solution is dilute, so there are not very many hydroxide ions. But the question is: Is it to be considered a strong or a weak base? Since chemists know that it is completely ionized, they consider calcium hydroxide to be a dilute solution of a strong base. *The extent of ionization is the basis for judging an acid as strong or weak, rather than its solubility.*

4-10· NAMING BASES

The rules for naming hydroxide-containing bases are simple. We give the name of the metal which the base contains and add the term hydroxide to it. Examples are: NaOH, sodium hydroxide; KOH, potassium hydroxide; Ca(OH)₂, calcium hydroxide.

4-11· WHAT IS A SALT?

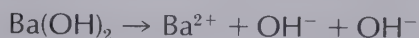
Thousands of different compounds called salts are known. The best known is common table salt, sodium chloride, NaCl. There are perhaps half a dozen exceptions, not many more, to the statement: *All salts are strong electrolytes.*

When sodium chloride is dissolved in water, there are no molecules of sodium chloride:

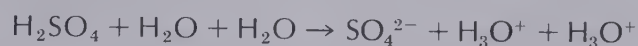


Actually, there are no molecules of sodium chloride in the solid, white, common table salt, either. Solid table salt is made up of sodium ions and chloride ions, not molecules. So, it is to be expected that it would be a strong electrolyte in water solution. Almost all salts are ionic solids like table salt, and they are also strong electrolytes.

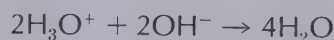
One way to make a salt is to mix a solution of an acid and a base. For example, suppose we wished to make the salt called barium sulfate, BaSO_4 . First, we would dissolve the base, barium hydroxide, Ba(OH)_2 , in water:



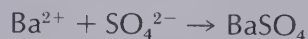
Next, we would dissolve sulfuric acid, H_2SO_4 , in water:



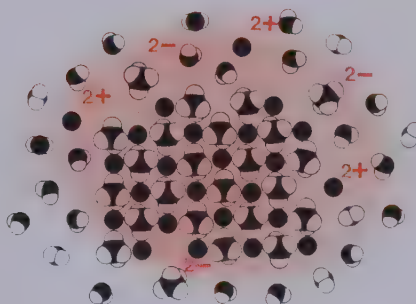
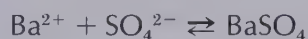
When these two solutions are mixed, the hydronium ions react with the hydroxide ions to form water:



The barium ions and sulfate ions react to form barium sulfate:



Barium sulfate is almost insoluble in water, so most of it precipitates out of the liquid, falling to the bottom of the test tube as a white solid. Since it is a salt, and is very slightly soluble in water, not quite all would form a solid. The part that remains in solution is all in the form of ions. Because a dynamic equilibrium is involved, the reaction equation should be:



To make sodium chloride, we would mix a solution of hydrogen chloride, HCl, with a solution of sodium hydroxide, NaOH.

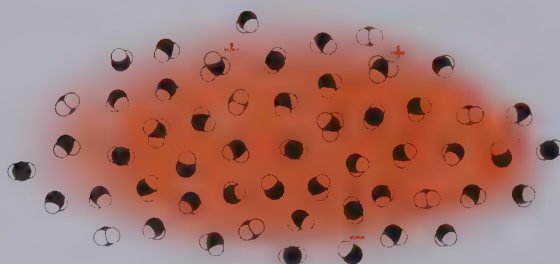
Salts can be thought of as being composed of two parts: the positive part from the hydroxide base and the negative part from the acid. Even though there are other ways to make salts, this is a convenient way to think of a salt. Salts are generally named on this same basis. First, state the name of the positive part, from the base, and then the name of the negative part, from the acid.

Problems

1. Write the equations for the reactions that take place when solutions of hydrogen chloride (called hydrochloric acid) and sodium hydroxide are mixed. In this case, the salt that is formed, NaCl, remains in solution as ions unless very concentrated solutions of acid and base are used.
2. Name the salts that result and write the equations for their formation, given the following information:
 - a. Solutions of hydrobromic acid, HBr, and potassium hydroxide, KOH are mixed.
 - b. Solutions of lithium hydroxide, LiOH, and acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ are mixed.

4-12. MEASURING THE HYDRONIUM ION CONCENTRATION IN SOLUTIONS

Pure water is a weak electrolyte. In water, by itself, there are a few hydronium ions and a few hydroxide ions and many water molecules:





Reading this equation from left to right, notice that one water molecule acts as a base and takes a proton; the other acts as an acid and gives up a proton. Reading from right to left, the hydroxide ion acts as a base, taking a proton from the hydronium ion, and the ions become water molecules. In pure water there is an equal concentration of hydronium ions and of hydroxide ions—not many of each compared to the number of water molecules, but the same number of each. Concentration is usually expressed as moles per liter of solution, as you learned in Chapter 3. Mole is a word for a number of particles just as dozen is a word for a number of oranges or eggs. When you weigh an amount of an element determined from the table of atomic weights, you are actually counting numbers of particles. If all eggs weighed the same, we could do this for eggs; some banks actually do count coins by weighing them, as you perhaps know. Mole is a much larger number than dozen. We will discuss it in detail later. For the moment, think of it as a number of particles.

In a liter of pure water there is 0.0000001 mole of hydronium ions and 0.0000001 mole of hydroxide ions present at ordinary temperatures (more than this, of each, at higher temperatures). It is troublesome to write 0.0000001 mole if you wish to express this number of moles of ions, so a shorthand scheme is used. We write “pH is 7,” where the H stands for the hydronium ion, the p tells us to count decimal places, and the 7 tells us to count seven decimal places. For the hydroxide ion, then, we would write “pOH is 7,” using the OH to signify the hydroxide ion. Generally, pH is used more than pOH. Let us consider pH in further detail.

In general, pH can have any value. By adding acid to pure water, we would change the hydronium ion concentration and express this as a pH different from 7. Or, by adding a base to pure water, we change the hydroxide ion concentration, and this makes the pOH different from 7. It also changes the hydronium ion concentration for reasons related to the dynamic equilibrium that exists in water. So, by adding a base to water, we change the pH from 7, also. For most purposes, it is sufficient to look at the details of the range of pH values from 0 to 15. The scale of pH range over these number values can be understood as representing a range of hydronium ion concentrations.

Each number going up on the pH scale represents a hydronium ion concentration just one-tenth as great as the preceding number. For example, the number 0 indicates a hydronium ion concentration of 1.0 mole per liter; the number 1 indicates a H_3O^+ concentration of 0.1 mole per liter; the number 2 indicates a H_3O^+ concentration of 0.01 mole per liter, and so on. Below 7, decreasing numbers indicate more H_3O^+ ions and stronger acidity. Above

7, as the H_3O^+ concentration decreases, the OH^- concentration is increasing. That is, the higher the number, the more basic the solution.

A summary of pH values in terms of hydronium ion concentration is given in Table 4-2.

The pH System of Indicating Acidity and Basicity			
Concentration of H_3O^+ Ions in Moles per Liter	Concentration Expressed Exponentially	Concentration Expressed as pH	
1.0	10^0	0	Increasing basicity ↑
0.1	10^{-1}	1	
0.01	10^{-2}	2	
0.001	10^{-3}	3	
0.0001	10^{-4}	4	
0.00001	10^{-5}	5	
0.000001	10^{-6}	acidic 6	↓ Increasing acidity
0.0000001	10^{-7}	neutral 7	
0.00000001	10^{-8}	basic 8	
0.000000001	10^{-9}	9	
0.0000000001	10^{-10}	10	
0.00000000001	10^{-11}	11	
0.000000000001	10^{-12}	12	
0.0000000000001	10^{-13}	13	
0.00000000000001	10^{-14}	14	
0.000000000000001	10^{-15}	15	

Table 4-2

Notice in the table that the pH is merely the indication of the placement of the decimal point. For example, suppose that we are thinking of a hydronium ion concentration of 0.01 mole per liter of solution. The decimal point in "0.01" is two places to the left of where it would be to express the whole number "1." From this we can tell that the pH is 2.

It is interesting to note that there are other pH values, such as 3.5, or 8.1; of course, you cannot move a decimal point three and a half places, or eight and one-tenth places, so you can see there is more to pH than what is stated here. Nevertheless, you could imagine that the decimal point was moved three and one-half places; or if it could be moved this way mathematically, by a clever trick involving logarithms (and it can be), the pH would then be 3.5 or some other number such as 8.1 or 9.8.

In many processes a small change in the pH of a solution turns out to be important. For example, the pH of your blood must be 7.4, plus or minus a very little, or death follows quickly. The pH of the blood is kept just right by dissolved substances called *buffers*. We will consider buffer solutions in Sec. 4-15. When you exercise vigorously, for example, carbon dioxide accumulates in the blood. This decreases the pH of your blood. Unless corrective steps are taken, the pH of your blood will get dangerously low.

Fortunately, your body can sense this increase in pH, and you start to breathe rapidly and deeply. This helps the lungs take the extra carbon dioxide out of the blood, exhaling it into the air, and the pH of your blood is changed to a safer value. But it takes a little time for the automatic operations that force you to breathe deeply to begin. Did you ever notice that as you run fast, you do not begin to breathe deeply until after you have run a while? Also, if you stop running, in many cases the body has not yet rid itself of all the extra carbon dioxide, so you must continue to breathe deeply for a bit longer. Even after you stop running, you often will still be breathing hard; you will say between puffs that you are “out of breath.” Actually, you are still getting rid of carbon dioxide. This is not the whole story on being out of breath, but this is one important part of the picture.

4-13· CHEMICAL INDICATORS

The chemist must have some means of determining whether a solution is acidic, basic, or neutral. Chemical indicators can serve this purpose. Essentially, *an indicator is a dilute, weakly acidic solution that changes color as the concentration of H_3O^+ and OH^- ions varies.* Three indicators often used in laboratory work are litmus, methyl orange, and phenolphthalein. Litmus is an organic dye which is derived from primitive plants called lichens. It is red in the presence of an acid and blue in the presence of a base. A memory device for accurate recall is to associate the letters *d* and *b*:

aciDs turn litmus reD

Bases turn litmus Blue

Methyl orange is an indicator which is yellow in basic solutions and red in acidic solutions. The pH range through which the change in color occurs is 3.1 to 4.4. Phenolphthalein is colorless in acidic solutions and pink in basic solutions, unless they are very basic, when the indicator becomes colorless again.

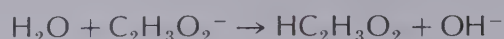
We will be using these three indicators quite frequently, so the pH range for them is listed for your information. Look at the color plate on page 121 for additional information on indicators.

pH Range of Common Indicators		
Indicator	pH Range in Which Color Changes	Color Change with Increasing pH
litmus	4.5 to 8.3	red to blue
methyl orange	3.1 to 4.4	red to yellow
phenolphthalein	8.3 to 9.8	colorless to pink

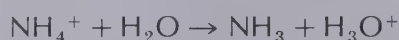
Table 4-3

4-14. HYDROLYSIS REACTIONS

Some ions react with water, as you have learned. The acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$, for example, is a good base. It can take a hydrogen ion from water:



This is a *hydrolysis reaction*; water behaved as an acid, the acetate ion as a base. The opposite can happen also; water acts as a base, and the ion as an acid. The ammonium ion, NH_4^+ , is an example:



Both of these are hydrolysis reactions. A *hydrolysis reaction* is a reaction between an ion and water, where the ion acts either as an acid or as a base.

Sodium acetate is a salt, as you can guess from its name. In water solution it forms ions, completely, but one of those ions acts as a base:



The acetate ion that is formed reacts with the water that is present in the solution, and a hydroxide ion is formed as one of the products:



Sodium acetate is the salt of the strong parent base, sodium hydroxide, and the weak parent acid, acetic acid. All salts whose parent base is strong and whose parent acid is weak will form ions in solution that are able to act as bases. Such salts will then cause the hydroxide ion concentration in water solution to increase. The pH of a solution of a salt of a strong base and weak acid will be greater than 7.

As an example of the opposite effect, consider the salt, ammonium chloride. This is the salt made by mixing ammonia water (a weak electrolyte and a weak base) with hydrochloric acid (hydrogen chloride in water solution), which is a strong acid. In water, ammonium chloride ionizes completely:



Then the ammonium ion reacts with a water molecule in the solution to form a hydronium ion as one of the products:



So, the pH changes to a lesser, more acidic value. All salts whose parent base is weak and whose parent acid is strong will behave in the same way.

Suppose that the parent acid and base of a salt are both strong; what happens then? Sodium chloride is an example:



Nothing further happens. The solution remains neutral. Sodium ion cannot act as an acid; it has no protons to lose; the same is true for the chloride ion. Neither ion acts as a base as we have learned earlier.

Suppose that the parent acid and base of the salt are both weak. Ammonium acetate is a good example. The ammonium ion will react with water,

forming hydronium ions as one of the products, and the acetate ion will react with the water, forming hydroxide ions as one of the products. One effect tends to increase the pH and the other to decrease it. The overall result is that not much change occurs in the pH. Usually, one of the two, the acid parent or the base parent, will be slightly weaker than the other, so a slight change in the pH, up or down, occurs. In the case of ammonium acetate, the parent acid and parent base are equally weak, so the effect is no change in pH.

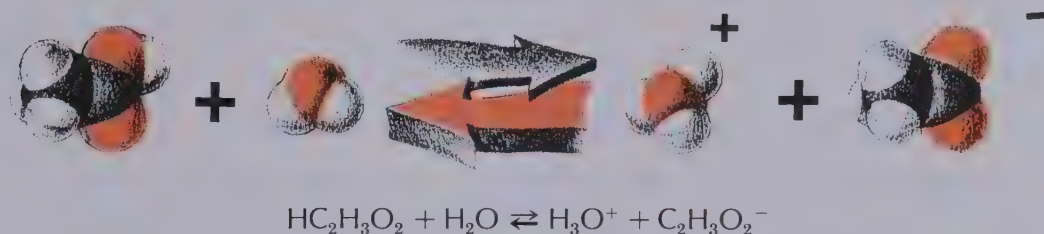
You can predict whether a salt will give a neutral, acidic, or basic solution in water by noting the strengths of the parent acid and base. Remember that the positive ion in a salt comes from the base and the negative ion from the acid. Three strong acids are: HCl, H₂SO₄, and HNO₃. Three strong bases are: NaOH, Ba(OH)₂, and KOH.

Hydrolysis reactions are very important in biological systems as well as in the chemistry laboratory. You will obtain more evidence of this when you perform Exp. 4-4.

4-15. THE COMMON ION EFFECT

An interesting application of Le Chatelier's Principle can be seen in connection with our study of weak electrolytes, such as acetic acid. We know that when acetic acid ionizes, hydronium ions and acetate ions are present in the solution in equal numbers. Since acetic acid is a weak acid, at equilibrium there are fewer ions than acetic acid molecules. What happens when we add another solution which also contains acetate ions? Sodium acetate is a strong electrolyte, ionizing completely. If we add this salt to an equilibrium solution of acetic acid, the concentration of acetate ions is greatly increased. This puts a stress on a system in equilibrium, and it will react in a manner to counteract the stress; in this case the system will act so as to use up acetate ions.

That is, in a solution of acetic acid, once we have some acetate and hydronium ions, a dynamic equilibrium of opposed equal rates is established:



When the sodium acetate is added, more acetic acid molecules are formed, since the added acetate ions are good bases. The concentration of hydronium ion is decreased, and the solution becomes less acidic. A new dynamic equilibrium is established with more acetic acid molecules present, fewer hydronium ions and, of course, some of the extra acetate ions still present as ions. The sodium ions that are also present do not get involved.

That is, to start with, the acetic acid molecules are in equilibrium with the hydronium ions and acetate ions; we have acetic acid molecules and only a

few of the ions. By adding more acetate (and sodium) ions, we put a stress on this equilibrium system, and it reacts so as to use up some of the added acetate ions. In doing this it also uses up some of the hydronium ions, and forms more acetic acid molecules, thus increasing the pH of the solution.

This is an application of Le Chatelier's Principle. The stress we put on the equilibrium system by adding more acetate ions is in part removed when the system itself uses up some of those added acetate ions. It is able to do this because the acetate ions are good bases, and ready to be converted into acetic acid molecules by picking up protons from hydronium ions.

The removal of hydronium ions (they lose their hydrogen ion part, and become water) makes the solution less acidic. Before adding sodium acetate, the pH is about 4 or 5, and after adding sodium acetate, it is nearer to 7.

This phenomenon is known as the *common ion effect* because acetate ion is common to both solutions, the acetic acid solution and the sodium acetate solution.

Buffer Solutions

An important application of the common ion effect is in the use of buffer solutions. *Buffers are solutions containing substances which control the pH of a system within certain limits.* The acetic acid-sodium acetate mixture is an example of a buffer. If extra OH^- ions are added to the solution, the H_3O^+ ions from acetic acid react with them; if an excess of H_3O^+ ions is added to the solution, the acetate ions react with them to form more acetic acid. In both instances a relatively constant pH is maintained.

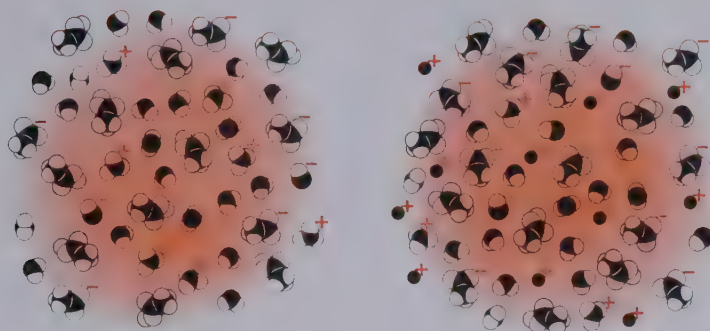
Biological systems depend upon the buffering action of different substances to maintain the delicate pH balance so essential to their function. The human blood system is an example. As we have pointed out, the blood of humans is maintained with surprising constancy at a pH of 7.4. Even within a given individual, the pH difference between venous and arterial blood does not vary more than about 0.02 units. Buffers in blood include several substances acting together, among which are proteins and the HCO_3^- ion.

4-16. APPLICATION OF LE CHATELIER'S PRINCIPLE

In our study of acids, bases, and salts we have encountered reactions in which Le Chatelier's Principle can be applied. We found that in hydrolysis reactions, it is the shift in the equilibrium and its effect upon H_3O^+ and OH^- ions in the water which causes the resulting solution to be either basic or acidic. If the dissolved salt forms ions that are neither bases nor acids, the small concentrations of H_3O^+ and OH^- present in the water itself are not changed, and the solution remains neutral.

In the common ion effect, Le Chatelier's Principle is applied. Acetic acid does not tend to ionize greatly in water; there is an equilibrium:





A solution of acetic acid before (left) and after (right) sodium acetate is added. The acetate ion is the common ion.

The concentration of hydronium ions can be reduced by adding more acetate ions. Acetate ions are called the common ions because they are present in both the solution of acetic acid and the solution of sodium acetate. As you know, sodium acetate ionizes completely in water:



The addition of excess acetate ions exerts a stress on the acetic acid equilibrium, and the system reacts in such a way as to relieve the stress by using up some of the extra added acetate ions. To do this requires that hydronium ions be removed by losing their hydrogen ion and becoming water molecules, and more acetic acid molecules are formed. When this happens, the acidity of the solution decreases, as you observed in Exp. 4-4.

Since the common ion effect can be used to control the pH of a system containing a weak acid or a weak base, we use this principle in buffer solutions. It was evident in your experimental work that a much larger volume of HCl solution or NaOH solution was required to change the pH of the buffered solution in Exp. 4-4.

Suggestions for Creative Work

1. It has been said that an increase in the acidity of the saliva indicates that one is in the first stages of catching a cold. Plan a series of investigations that may help you to test the validity of this statement.
2. Plan an experiment to determine the freezing point or the boiling point of a water solution of either a molecular or ionic solute.
3. Devise an experiment to determine the molarity of a sodium hydroxide solution whose concentration is not known.

Suggestion for Creative Writing

1. Write a research paper reporting on the action of buffers in the human body.
Note: This is not original research, but will be most informative if you do sufficient reading. You might also talk with your doctor about sources of information.

Practice Exercises *(Answers on p. 312)*

1. For each of the following 1-M solutions, tell whether you would expect it to be acidic, basic, or neutral.
a. KNO_3 b. $(\text{NH}_4)_2\text{SO}_4$ c. KCl d. Na_2CO_3 e. BaCl_2
2. What is the expected pH of the following solutions of nitric acid?
a. 0.1 M b. 0.0001 M c. 1.0 M
3. Cite one example of a buffer solution and explain why it acts as a buffer.
4. What is the modern definition of an acid? a base? Cite one example of each.
5. Which is the stronger base, water or ammonia (NH_3)? Give reasons for your answer.
6. Why do bases feel slippery?
7. Given samples of two colorless liquids, what test would you use to determine whether each was an acid or a base?
8. Name the following:
a. NaOH e. H_2CO_3
b. HNO_3 f. CuSO_4
c. $\text{HC}_2\text{H}_3\text{O}_2$ g. KBr
d. KOH
9. Given: $\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$
Apply Le Chatelier's Principle to explain the effect upon the equilibrium system that adding a few drops of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$) solution would have and cite reasons for your answer.
10. Why is hydron paper preferable to litmus paper for most experiments?
11. Explain the differences between a strong electrolyte and a weak electrolyte.
12. (Multiple Completion; see special directions in Appendix 13)
Weak electrolytes include
 1. hydrochloric acid, HCl
 2. acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$
 3. potassium hydroxide, KOH
 4. tap water

Self-Test *(Answers on pp. 312, 313)*

1. Define:
 - a. acid
 - b. base
 - c. electrolyte
 - d. salt
 - e. chemical indicator

2. Name the following acids
 - a. HCl
 - b. H_2SO_4
 - c. H_2S
 - d. HBr
3. Name the following bases:
 - a. $\text{Ca}(\text{OH})_2$
 - b. $\text{Ba}(\text{OH})_2$
 - c. $\text{Mg}(\text{OH})_2$
4. Name the following salts:
 - a. NaNO_3
 - b. MgCl_2
 - c. CaSO_4
5. State whether each of the following salts can be expected to be acidic, basic, or neutral in water solution:
 - a. BaCl_2
 - b. NaCl
 - c. KNO_3
 - d. $\text{KC}_2\text{H}_3\text{O}_2$
6. For each pH given here, write the hydronium ion concentration of the solution:
 - a. $\text{pH} = 8$
 - b. $\text{pH} = 2$
 - c. $\text{pH} = 7$
 - d. $\text{pH} = 1$
7. Explain why most acids, bases, and salts are electrolytes, while carbon tetrachloride is not.
8. State the general properties of acids and bases.
9. Describe one method by which you could prepare a salt in the laboratory.
10. Why is HCl a strong electrolyte? Why is ammonia water a weak electrolyte?
11. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION	REASON
Water is a stronger base than ammonia, NH_3 ,	Because ammonia takes a proton from water to form NH_4^+ ions and OH^- ions.

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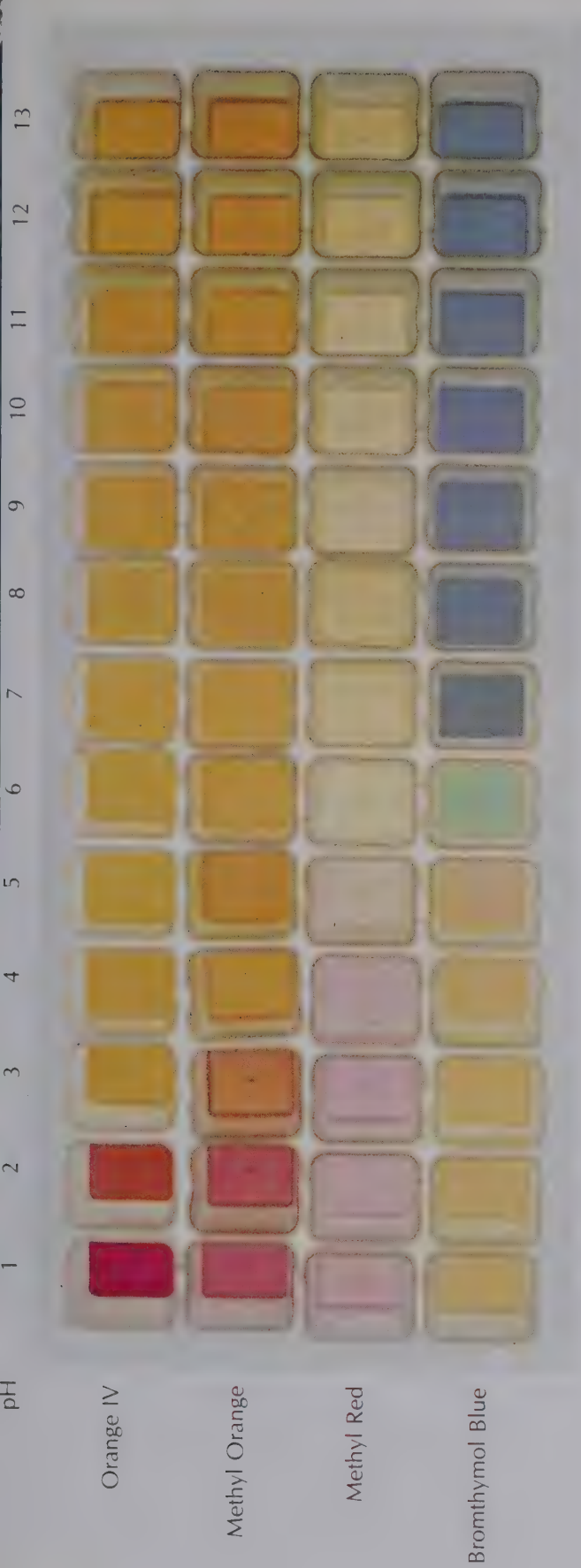
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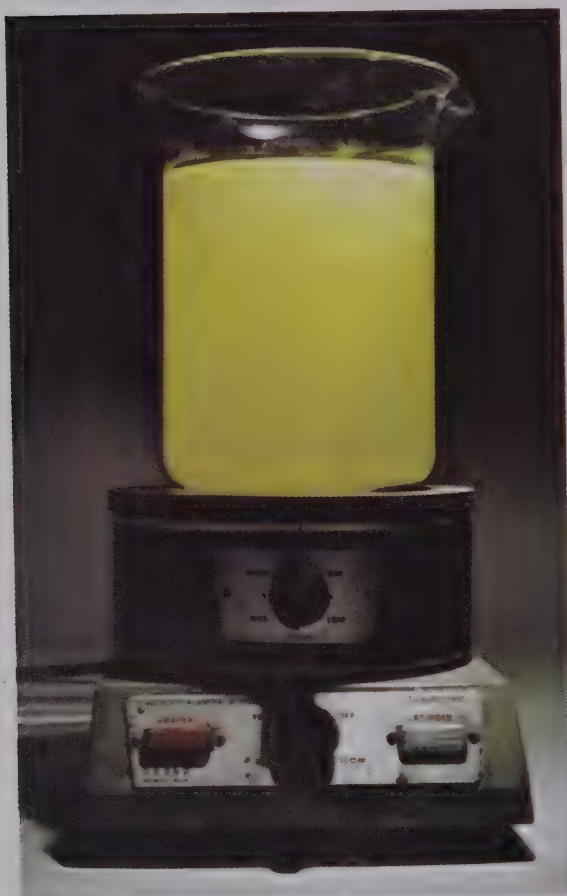
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Very fine chapter on acids, bases, and salts with numerous illuminating illustrations.





Solutions of Bromine (left) and Iodine (right) in carbon tetrachloride; the appearance of positive tests for Br_2 and I_2 .





Hydrated Chromium Nitrate
 $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Ammonium Dichromate
 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

Potassium Chromate
 $\text{K}_2\text{Cr}_2\text{O}_7$

Hydrated Cobalt Chloride
 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Nickel metal Ni

Nickel Sulfate NiSO_4

Copper metal Cu

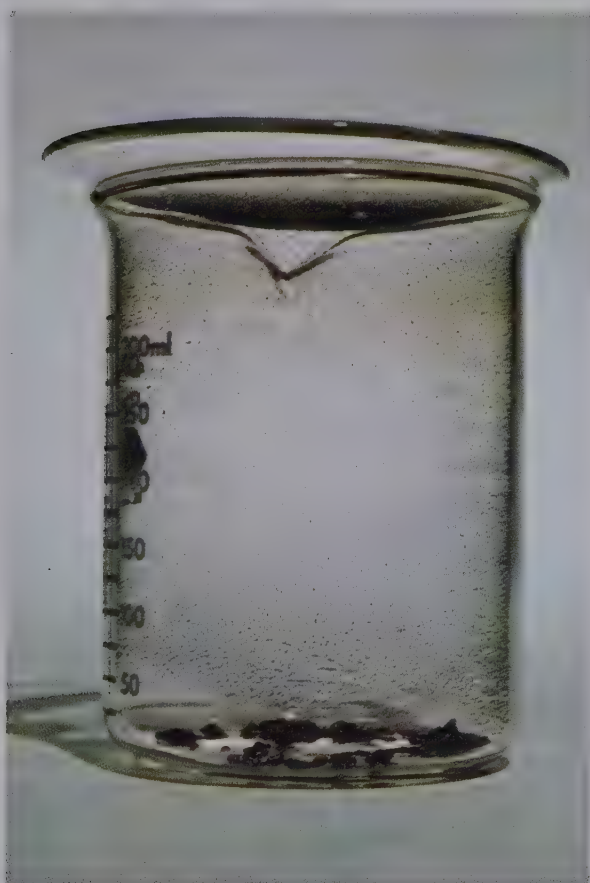
Cupric Chloride CuCl_2

Hydrated Copper Sulfate
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Sulfur S_8

Bromine Br_2

Iodine in both crystal and vapor form.



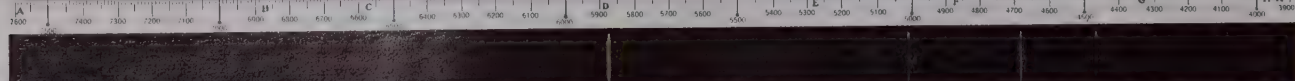
Chlorophyll is the
source of the green
color in a leaf.



Period 1



Hydrogen



Helium

Group Ia



Lithium

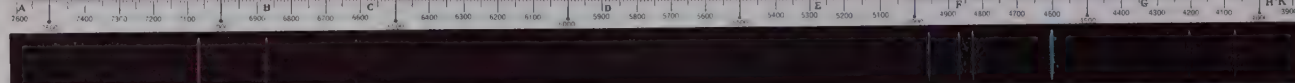


Sodium

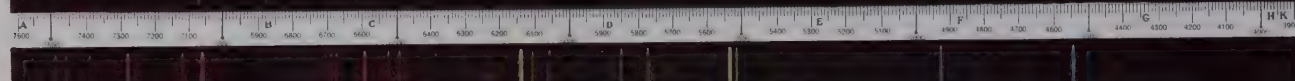
Group IIa



Calcium



Strontium



Barium

Group IIb



Cadmium



Mercury

Continuous spectrum



Solar absorption spectrum

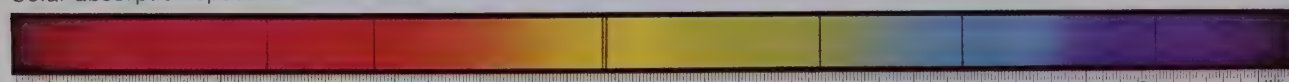
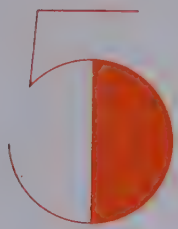


Plate 25 Incandescent solids, liquids, or gases under high pressure give off a "continuous" spectrum like that shown here from the tungsten filament of an ordinary light bulb. Passing an electrical discharge through gases at low pressure causes spectra composed of discrete bright lines on a dark background. The principal lines of some bright-line spectra are shown arranged according to their grouping in the periodic chart (see list at right).

Although the spectrum of the sun may look like a continuous spectrum, on closer examination, many dark lines (only a few of which are indicated here) can be seen. Note that the position of these lines corresponds exactly to the position of bright lines in the bright-line spectra. These absorption lines occur when light passes through a gas cooler than the gas emitting the light. This cool gas absorbs the same frequencies it would ordinarily emit at higher temperatures.

After examining these four pages of color photos, what can you suggest about the relationships between chemical materials, light, and color?



THE DEVELOPMENT OF ATOMIC THEORY

OBJECTIVES:

By the time you have completed your study of Chapter 5, you will be expected to demonstrate acceptable performance on the following objectives.

1. Compare the "black box" experiment to unsolved problems in modern science and list five of these unsolved problems.
2. Discuss Dalton's model of the atom and explain why it has been modified.
3. List three reasons why Dalton's work was important to the development of science.
4. Describe Rutherford's alpha scattering experiment and discuss how the results led to his proposal of the nuclear model of the atom.
5. Explain how Dalton's atomic theory predicted the existence of compounds such as carbon monoxide, CO, and carbon dioxide, CO₂.
6. Draw a typical representation of a wave and label its parts: crest, trough, amplitude, wave-length.
7. Define frequency as applied to waves and explain how frequency is dependent upon wavelength.
8. Explain how radiant energy waves differ from sound or water waves.
9. Explain how a continuous spectrum is different from a line spectrum.
10. Explain the causes of the lines in the hydrogen spectrum.
11. Discuss the contribution of Max Planck to our present understanding of light.
12. Summarize the contributions of any three scientists whose work led to our present understanding of atomic structure.
13. State the major contribution of each of the following scientists to the development of the modern atomic theory:

a. Democritus	f. Millikan	j. Soddy
b. Newton	g. Becquerel	k. Bohr
c. Thomson	h. Rutherford	l. Planck
d. Avogadro	i. Richards	m. Einstein
e. Dalton		
14. Discuss the interdependence of fact and theory.
15. State at least three reasons for the need to study the development of atomic theory in a historical context.
16. Identify the following ions by any appropriate laboratory method:

a. sodium, Na ⁺	e. barium, Ba ²⁺	i. nickel, Ni ²⁺
b. potassium, K ⁺	f. calcium, Ca ²⁺	j. cobalt, Co ²⁺
c. copper, Cu ²⁺	g. aluminum, Al ³⁺	k. chromium, Cr ³⁺
d. strontium, Sr ²⁺	h. zinc, Zn ²⁺	l. manganese, Mn ²⁺
17. Summarize the model of atomic structure proposed by Bohr.

SUGGESTED ORDER OF STUDY

Note: You are expected to do outside reading, free labs, and other forms of creative work at appropriate times. These activities should be placed in this suggested schedule as you see fit.

1. Perform Exp. 5-1. ✓
2. Study Secs. 5-1 through 5-4.
3. Read the biographies of some of the scientists discussed in these sections. (See Bibliography.)

4. Observe the demonstration on the electrical nature of matter.
5. Study Secs. 5-5 through 5-9. Do related readings in resource books.
6. Perform Exp. 5-2. ✓
7. Read the bibliographic references by Gale and Wallace if they are available.
8. Perform Exp. 5-3. ✓
9. Study Secs. 5-10 through 5-14.
10. Do the Practice Exercises and review as needed.
11. Take the Self-Test; review as needed.
12. Take test on Chapter 5.

5-1 • THE ROLE OF IMAGINATION IN SCIENCE

Imagination is an indispensable tool for both scientist and student. It includes the abilities to view observed facts in a variety of ways, to construct mental patterns, and to see unexpected possibilities in familiar ideas. Each person's attitudes, memories, and beliefs determine how he interprets an observation. A controlled experiment yields facts from which logical conclusions can be drawn, yet the very recording of a fact involves the whole of our previous experience. Therefore, your past experience will have much to do with how you perceive an experiment.

To test this statement, let us review a few observations from a "black box" activity reported by one student:

1. My box seems to contain two objects.
2. One object rolls like a marble.
3. The spherical object sounds like a marble when it strikes the side of the box and the other object inside the box.
4. Another object is heavy and metallic. It slides and does not roll.
5. The metallic object responds to a magnet.
6. From testing with a magnet, it seems that the metallic object is about 4 cm long and 2 cm wide.

It is obvious that previously learned concepts of mass, length, and shape were employed by the student reporting these observations. Memory of how glass sounds when it strikes metal or wood and practice in estimating size were necessary in making useful observations. This example emphasizes that the way we think in dealing with any situation includes previous learning. By using acquired knowledge plus imagination, it is not difficult to arrive at an acceptable model for the contents of the box.

This same procedure characterizes the work of a scientist. A collection of facts is not science. Facts must be studied and regularities determined. After this is done a model, or analogy, must be devised to make a given situation more meaningful. The beginning student of chemistry and the most advanced theoretical physicist employ models to aid understanding. *While models are helpful, we must never lose sight of the fact that they are only models.* They help us understand the realm of nature, which is unseeable but, nevertheless, very real and significant.

Your experience in discovering the pattern and contents of the “black boxes” without being able to look into them should give you confidence in the value of indirect evidence. This simple activity can help you to appreciate the importance of past experience and imagination in interpreting observations made under new conditions. Nowhere is this more evident than in the development of the atomic theory.

5-2 · THE ATOMIC THEORY

The theory of the structure of matter has been developing for more than 2500 years. In fact, it is still in the process of development. Each generation makes new discoveries which require modification of the theory. To the serious student of science, it is important to trace the devious path by which we have arrived at the modern concept of atomic structure. To the casual student of science, it is perhaps even more important to understand how science grows. Mistakes and incorrect conclusions are an integral part of the growth of any human endeavor. Science is a human endeavor. Therefore, we will explore briefly the chronological development of the modern atomic theory for the structure of matter. Not only will this information make the theory more meaningful in its present form, but this approach will serve to illustrate (1) how scientists accumulate and interpret facts, (2) how they construct a reasonable model and employ it as long as it is useful, (3) how they modify it as new discoveries are made, and (4) how they invent theories to explain what has been observed.

Contributions of the Early Greeks

Man has speculated about the structure of matter from earliest recorded history. Many of the very early ideas were the result of thinking rather than of experimentation. In 450 B.C., Democritus, a Greek philosopher, first proposed that matter is composed of atoms. The word *atom* comes from the Greek *atomos*, which means “indivisible.” He considered the atom to be both indivisible and indestructible. This represented a compromise in the old philosophical argument about the limit to which matter could be divided. It permitted man to think of matter as being divisible beyond his ability to see, but still as having an ultimate unit which could not be further subdivided. This early concept of the atom, however, is quite unlike the modern concept. Aristotle (384–322 B.C.), an extremely influential Greek scholar, was among those who never accepted the atomistic concept of matter.

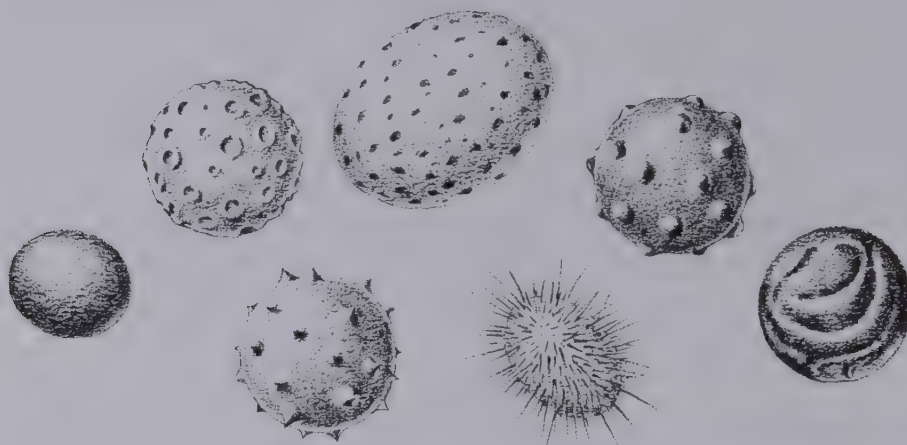
The atomic idea was generally regarded as atheistic because it attempted to explain matter on the basis of structure and not in terms of a Creator. Sir Isaac Newton (1642–1727), English physicist, solved the problem by accepting the atomistic view of matter while at the same time rejecting atheism. Newton contended that “the Deity created the World Machine and that by His Pleasure it could run without continual intervention.”

5-3 · DALTON'S ATOMIC THEORY

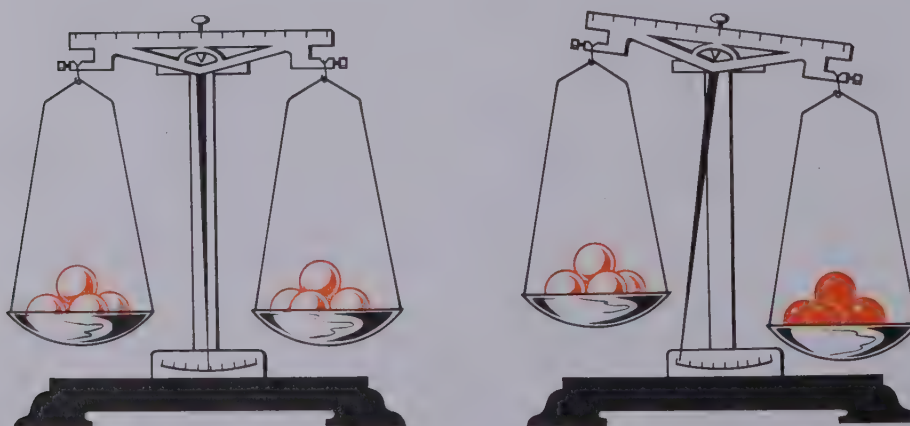
It was John Dalton (1766–1844), English schoolmaster, who first proposed a formal statement of an atomic theory. He was not particularly adept at performing experiments, but was gifted with the unusual ability to form mental pictures and to construct physical models. He used small spheres to teach his theory, much as we use Styrofoam balls today. His total work, *A New System of Chemical Philosophy*, was published in two parts in 1808 and 1810.

The major points of his atomic theory were:

1. All matter consists of invisible particles called atoms.
2. The atoms of a given element are alike in every respect, especially weight.
3. Atoms of different elements are different in every respect, including weight.
4. Chemical changes result from the combination of atoms of different elements.
5. Atoms cannot be divided into smaller parts, even in the most violent reaction.



Dalton believed atoms of different elements were different in every respect.



- (left) Atoms of the same element were believed to have the same weight.
(right) Atoms of two different elements were believed to differ in weight.

The First Attempt to Determine Atomic Weights

Dalton believed that atoms had weight and that they were too small to weigh individually. They were also too small to see and count. For example, one of the easy ways to weigh a small object, such as a penny, is to count out a dollar's worth of pennies and to weigh them all, and then divide by 100 to get the weight of one penny. But this cannot be done with atoms; they are too small to count. Still, Dalton wanted to determine the weight of atoms. You can see that he had a problem. He never did get his problem solved. Scientists did not figure out how to actually get the weight of an atom until about one hundred years after Dalton first considered the problem. So, how did Dalton handle this problem?

Let us set up an imaginary problem something like Dalton's problem. Suppose you had a box, something like your black box, and you filled it with a couple of handfuls each of black buttons and white buttons. You weighed all the black buttons together before you put them in, and found that they weighed 8 ounces; but you did not count them, you only weighed them. Similarly, without counting, you weighed the white buttons; together they weighed 1 ounce.

Now, if we ask the question, how much does one white button weigh, or how much does one black button weigh, we know that we cannot answer the question. Let's ask a different question: How much more does a black button weigh than a white button? You can see that we cannot answer that question, either. We need more information, and we do not have it.

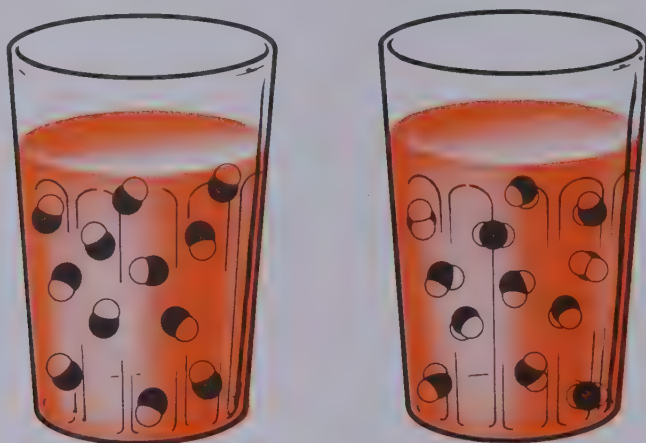
When a scientist, such as Dalton, faces a question like this where more information is needed and cannot be found, the scientist invents information. We will invent some information. We will say that there are as many white buttons as black buttons in the box. This information is perfectly useless as good information since we simply invented it. But, if we are willing to assume that it is good information, we can figure out that one black button is eight times heavier than one white button. Of course, we could invent some other information instead. We could say that there are twice as many white buttons as black buttons in the box. If we assume this is good information, now how much more does one black button weigh than one white button? With a little thinking and scribbling with pencil and paper, you can figure out that one black button would be 16 times heavier than a white button.

Now, for buttons in boxes this kind of silly invention of information has gone far enough. What did Dalton really do?

Dalton had some information about many different substances. For example, he knew from studies made by other scientists that water was composed of hydrogen and oxygen. When the weight of hydrogen and of oxygen obtained from the decomposition of any sample of water was measured by careful work in the laboratory, the results always came out the same: The oxygen weighs 8 times as much as the hydrogen with which it is associated in water. For nine ounces of water, for example (this is a little more than a cupful); it always came out 8 ounces of oxygen and 1 ounce of hydrogen.

Dalton already had the idea that water particles had both kinds of atoms,

hydrogen and oxygen. If each particle of water contained one atom of hydrogen and one atom of oxygen, then the number of atoms of hydrogen would be the same as the number of atoms of oxygen in the cupful of water. So, if this is correct, the formula for a water particle, a molecule of water, would be HO; the H stands for one atom of hydrogen; the O stands for one atom of oxygen; the HO stands for one molecule of water.



Is water HO (left) or H_2O (right)?

This is not too bad when you stop to think that we started with only a little bit of really good information, 8 ounces of oxygen and 1 ounce of hydrogen in 9 ounces of water. All the rest—matter consists of indivisible particles called atoms, and in the water molecules there is one atom each of oxygen and hydrogen, and so on—is simply invented. Yet, by using his imagination in this way, right or wrong, Dalton could say that an atom of oxygen is eight times heavier than an atom of hydrogen.

Today, we are pretty sure that the formula for water is H_2O ; there are two atoms of hydrogen and one atom of oxygen in each molecule of water. This means an oxygen atom is 16 times heavier than an atom of hydrogen. You should remember, though, that even today, when we have much more certain information from our laboratory work, there is still a considerable portion of invented ideas, called theories; so, science is not as sure about everything as some people seem to think it is.

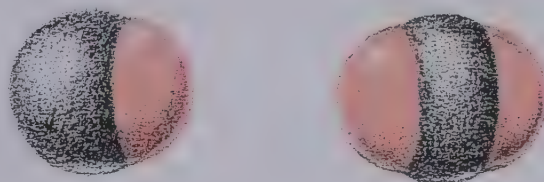
You might wonder why Dalton invented HO for water; why not H_2O , or HO_2 , or even something else, such as H_3O ? In his laboratory reports, which you can read about in books on the history of chemistry, Dalton said that he considered this. However, since he had no other information about what a molecule of water might be, he took the simplest as the best for the time being, one atom of each. When you stop to think about it, this was reasonable even though today we would say it was wrong.

So, Dalton continued to think about his atomic theory. From weight measurements of the elements in many different kinds of substances, and by assuming one-to-one associations of atoms in each substance, Dalton was able to calculate several weights of one kind of atom compared to another. He called these weights atomic weights.

Now, if one atom of an element would combine with one atom of another

element to make a molecule, it might be possible, Dalton also thought, that in some cases the same two elements might form more than one compound. For example, two different compounds of carbon and oxygen are known. In one of these, if we have 7 ounces of the compound, we find that it has in it 3 ounces of carbon and 4 ounces of oxygen. Today, this compound is known as carbon monoxide; it happens to be a very poisonous substance. The other compound is different; it is not poisonous although it can cause suffocation; it is called carbon dioxide. Eleven ounces of carbon dioxide contains only 3 ounces of carbon but 8 ounces of oxygen.

How can this be? In one case 3 ounces of carbon and 4 ounces of oxygen; in the other 3 ounces of carbon and 8 ounces of oxygen. Dalton said that in the first compound, the poisonous one, each molecule has one atom of carbon and one atom of oxygen. The formula is CO . Since the other has



twice as much oxygen for the same amount of carbon, it has two atoms of oxygen for each atom of carbon. It has the formula CO_2 . This argument helped to convince many other scientists of those days that Dalton's atomic theory might be correct. It explained how it could be that for the same weight of one element, carbon, there was exactly twice as much oxygen in one compound as in the other. About the only way there could be exactly twice as much oxygen by weight would be that there were exactly twice as many atoms of oxygen for each atom of carbon. This is not a proof of the atomic theory, but it sure makes it hard to think of another explanation!

In other books you can read about the Law of Definite Proportions or the Law of Definite Composition or the Law of Fixed Composition or the Law of Multiple Proportions. When you do, you will recognize that those books are talking about the same things we have talked about here. We do not think it is necessary, although it is perhaps helpful, to know the names of these so-called laws. It is more desirable that you know what Dalton thought and how he got around the difficult problem of insufficient information by inventing his own, and that he tried to be sure that what he did invent was reasonable.

The Importance of Dalton's Contributions

The influence of Dalton's work on science was very great; it made the concept of atoms real and gave meaning to the laws of chemical combination. However, it was also of tremendous significance in other ways, namely:

1. It provided a framework for organizing many previously unrelated facts.
2. It gave the scientific world a conceptual scheme which was both simple and workable.
3. It opened up new fields for research, particularly in the realm of combining ratios and determining atomic weights.

4. It provided a basis for predicting possible formulas for compounds.
5. It provided a way to visualize and think about substances and the way they reacted.

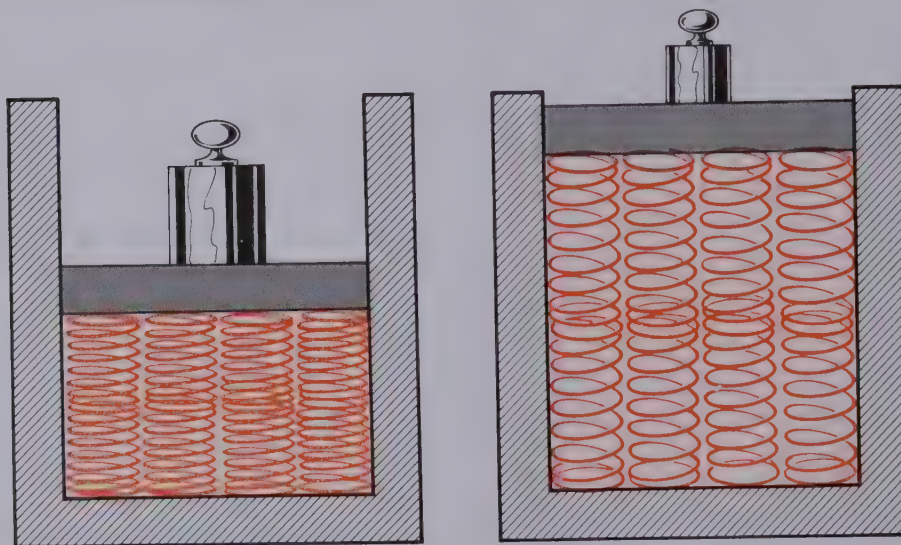
5-4. CONTRIBUTIONS TO ATOMIC THEORY FROM THE STUDY OF GASES

In 1643, Evangelista Torricelli, an Italian physicist, invented the barometer. With this instrument he measured the pressure that air exerts upon the earth. In his study of atmospheric pressure, Torricelli came to realize that we live at the bottom of a sea of air.

In 1660, Robert Boyle, an English physicist, demonstrated quantitatively that if a given mass of gas is trapped in a tube at constant temperature, any increase in the volume of the tube results in a decrease in the pressure the gas exerts. Conversely, if the volume of the tube is made smaller, the gas exerts greater pressure.

About 1790, Jacques Charles, a French physicist, discovered that when a given sample of gas is heated at constant pressure, its volume increases in direct proportion to the rise in temperature. Once observations are made, the scientist begins to search for a suitable explanation. As early as 1662, Boyle offered two explanations for the behavior of gases. Both were atomistic.

One explanation, known as the static model, compared the particles of a gas to little springs which are in contact with each other and are compressible. The other explanation proposed by Boyle, called the kinetic model, viewed gases as being composed of separate particles in a fluid which kept them in a constant state of motion.



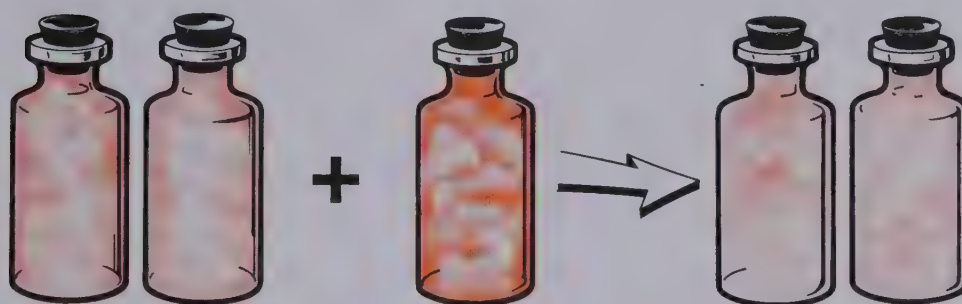
A static model for a gas might look something like this.

The Law of Combining Volumes of Gases

As Dalton continued to use the rule of greatest simplicity in determining relative atomic weights, it became apparent to him that inconsistencies were bound to arise. He had found by his methods that the formula for water could

be H_2O , HO_2 , or HO . Water is composed of 1 part by *weight* of hydrogen and 8 parts by *weight* of oxygen. If he assumed that H_2O was the correct formula, then the relative weights for hydrogen and oxygen would be 1 and 16; if the formula were HO , then the relative weights would be hydrogen, 1, and oxygen, 8.

In 1808, the results of experiments conducted by Gay-Lussac of France revealed that when oxygen and hydrogen are ignited to form water vapor, the *volume* of hydrogen to oxygen was always 2:1. He knew from the work of Boyle that all gases exhibit similar properties when subjected to pressure. Charles' experiments indicated that all gases behave similarly when heated or cooled. Therefore, Gay-Lussac assumed that all gases combine with each other in the simplest proportions possible. He noted from his own work and from the experiments of others that the ratio between the volumes of the combining gases and their products may be expressed as small whole numbers. This is known as the *Law of Combining Volumes*.



Dalton's Objections

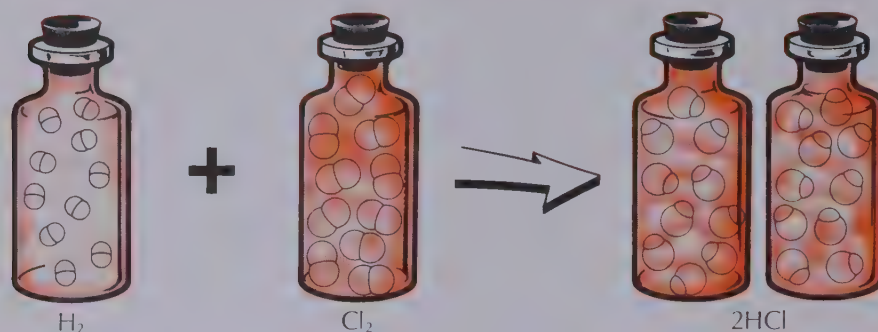
Dalton objected strongly to the ideas set forth by Gay-Lussac for several reasons. Dalton had done extensive work on the composition of air. He had found that, despite the fact that air is made up of several gases of different densities, it is remarkably homogeneous. His explanation for these observations employed a static model. Dalton believed that gas particles were in constant contact with one another, that the size of the particles differed with the kind of gas, and that the particles were at rest. To accept Gay-Lussac's concept of combining volumes meant that Dalton would have to reject his notion that the atoms of different elements must be of different sizes, and also his static model for gas behavior.

In 1811, a publication appeared that resolved the apparent conflict between the observations of Gay-Lussac and Dalton's theory.

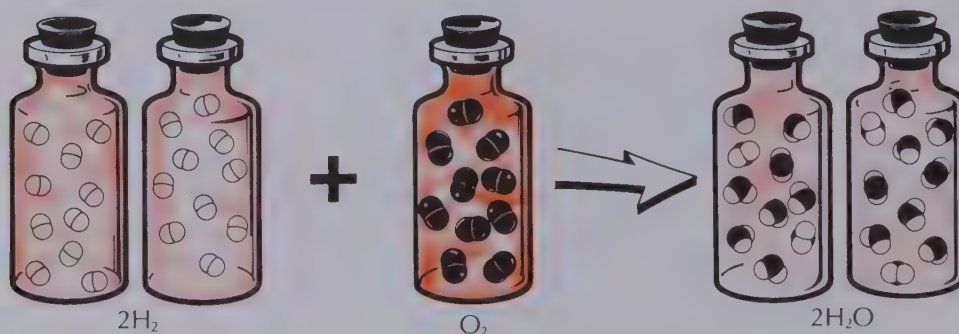
Avogadro's Theory

Amedeo Avogadro (1776–1856), an Italian physicist, proposed that units of gases were not necessarily atoms, but molecules. He coined the word *molecule* from the Latin term meaning "cluster." His work confirmed that of Gay-Lussac and resulted in his famous hypothesis: *equal volumes of gases at the*

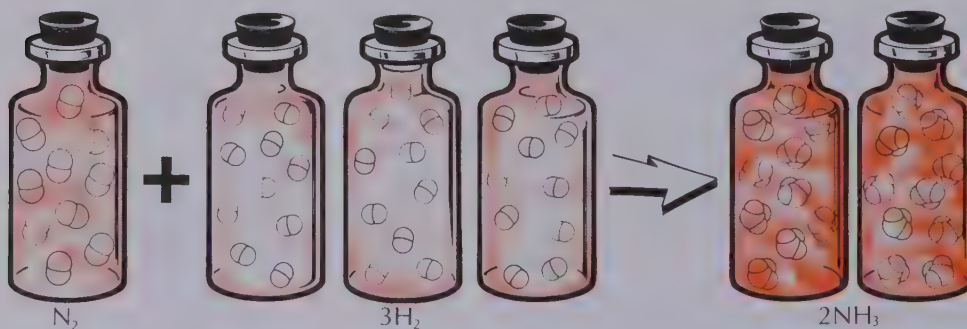
same temperature and pressure contain equal numbers of molecules. Since nothing was known then about atomic structure, Avogadro's statement was based upon intuition. His hypothesis has since been confirmed by many experiments and is now accepted and called Avogadro's Theory.



One volume of hydrogen plus one volume of chlorine yields two volumes of hydrogen chloride.



Two volumes of hydrogen plus one volume of oxygen yields two volumes of water.



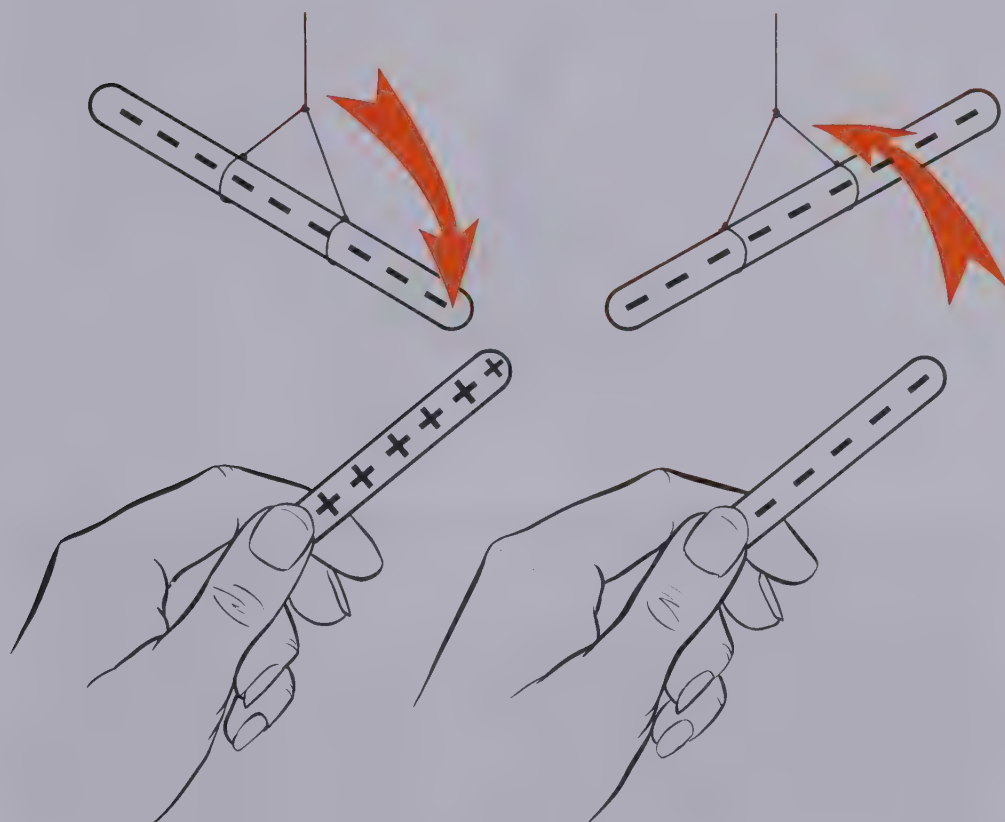
One volume of nitrogen plus three volumes of hydrogen yields two volumes of ammonia.

Thus, we find a recurring theme in the development of science: men with imagination very frequently advance an idea that seems absurd at the time, but which later is verified and accepted.

By the late nineteenth century, evidence for the existence of atoms was well established, but little was known about the structure of the atom itself. We will now give our attention to key experiments which led to the present concept of atomic structure.

5-5. THE ELECTRICAL NATURE OF MATTER

Since ancient times it has been known that when certain substances are rubbed briskly with cloth, they are capable of attracting and holding tiny bits of paper. You have observed that rubbing a rubber rod with fur causes it to attract pieces of paper. When a balloon is rubbed, it will cling to the wall for a time. You have also observed that when a charged rod is brought near an electroscope, the leaves move apart. Two charged rubber rods repel each other, and two charged glass rods repel each other. But if a charged glass rod is brought near a charged rubber rod, the two rods attract each other.

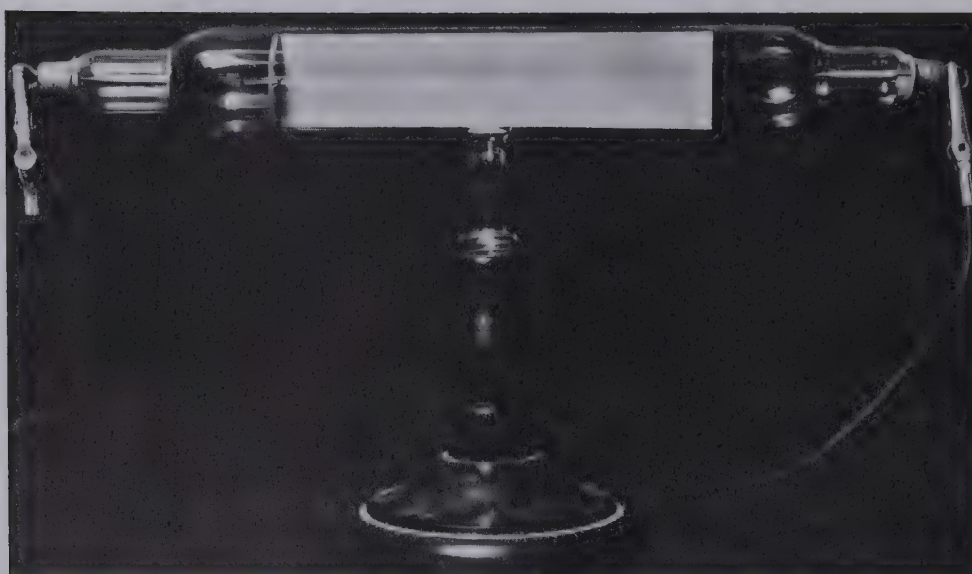
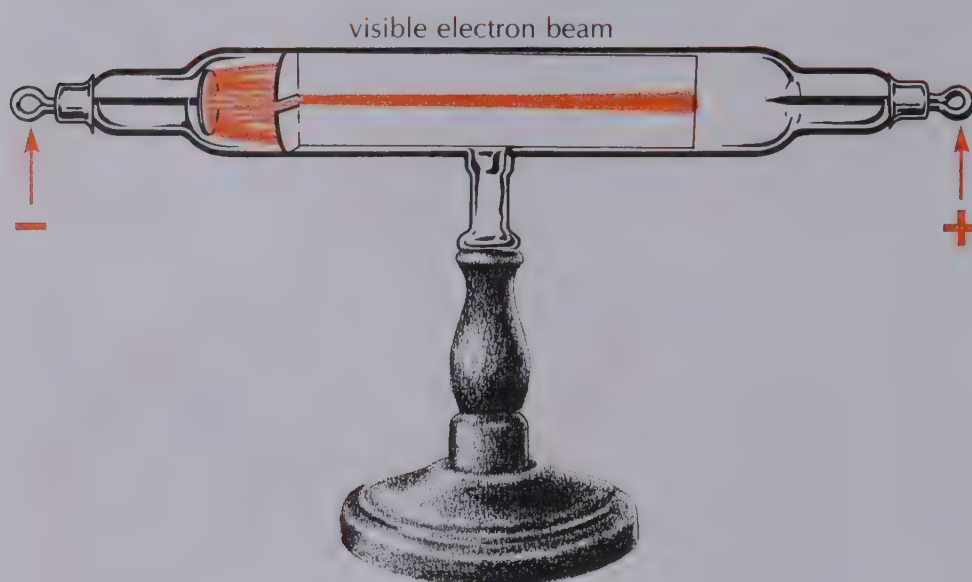


So far as we know today, there are only two kinds of electrical charge: positive and negative. The kind produced on the rubber rod is called negative, and the kind on the glass rod is called positive. Ordinary matter is neutral; that is, it contains equal amounts of negative and positive charges. Knowing these facts, it became the problem of the scientists to explain them.

The Discovery of the Electron

During the latter part of the nineteenth century, the behavior of gases carrying an electric current was investigated. The tubes used in such studies were

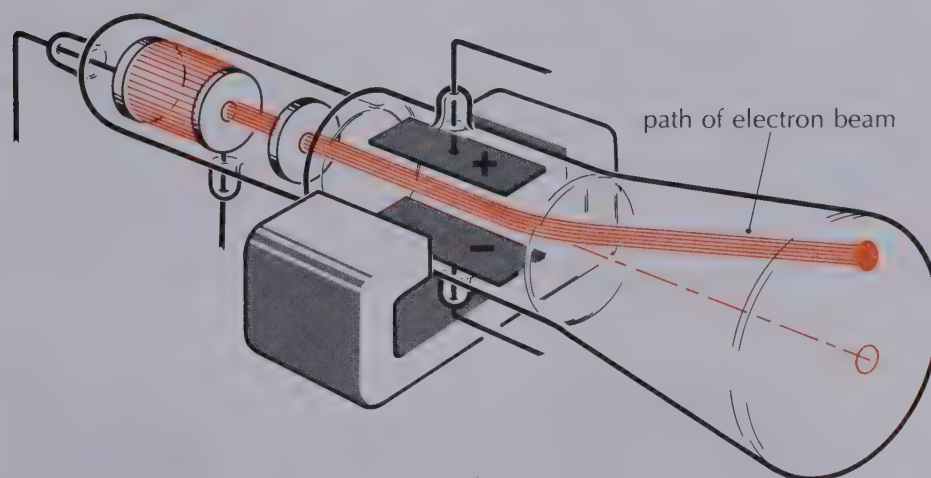
similar to present-day vacuum tubes. If you look at a vacuum tube when a radio or TV set is turned on, you will see a bluish glow. As physicists studied this phenomenon, they concluded that it was caused by rays coming from the negative pole in the tube. Since the negative pole of an electric cell is called



A cathode ray tube in operation.

the cathode, these rays were named *cathode rays*. J. J. Thomson (1856–1940), an English physicist, performed a series of experiments to investigate the behavior of these cathode rays. He announced his results in 1897 and was later awarded a Nobel Prize for his work. He found that both electric and magnetic fields caused the rays to be bent from their path. Since light is not affected by electric or magnetic fields, he was led to believe that the cathode rays must be matter. He further showed that positive particles were bent in the opposite direction from negative particles and that cathode rays were bent in the same manner as negative particles, and so they must, indeed, be negative. He called these negative particles *electrons*.

Thomson was able to determine the ratio of the mass of the electron to its charge. In 1909, Robert Millikan, an American physicist, determined the charge on the electron. By combining the results of Thomson and Millikan, the actual mass of the electron was calculated. It turns out to be $1/1840$ of the mass of a hydrogen atom.



A schematic of the apparatus used by Thomson to determine the ratio of mass to charge for the electron.

Thomson, in another series of experiments, found that when light of very high energy strikes zinc and other metals, negatively charged particles are given off by the metal. This is known as the *photoelectric effect*. He showed that these particles exhibited the same behavior as the particles in cathode rays. This was an important advance because it provided evidence that electrons can be obtained from different kinds of matter in different ways. This led to the conclusion that electrons are fundamental parts of atoms. It also showed that light and electrons interact. In the light of such evidence, the indivisible atom proposed by Dalton had to be modified to include the newly discovered facts.

5-6. THE THOMSON MODEL OF THE ATOM

The model of the atom proposed by Thomson was inadequate, even to Thomson, but it was useful because it represented the first attempt to introduce electrons into the atomic concept. Thomson described the atom as being

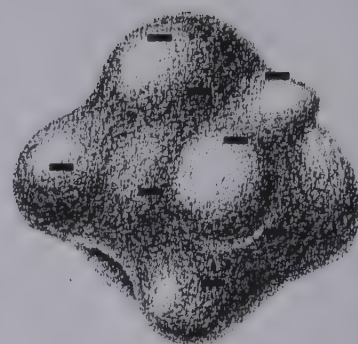
a positive globule in which electrons moved back and forth. The model may be compared to a bowl of gelatin fruit salad. The gelatin represents the globule of positive electricity, and the fruit represents the electrons. Thomson even went so far as to say that the periodic recurrence of similar properties of different elements might be related to different electron patterns in the atoms.

5-7 • RADIOACTIVITY AND THE NUCLEAR ATOM

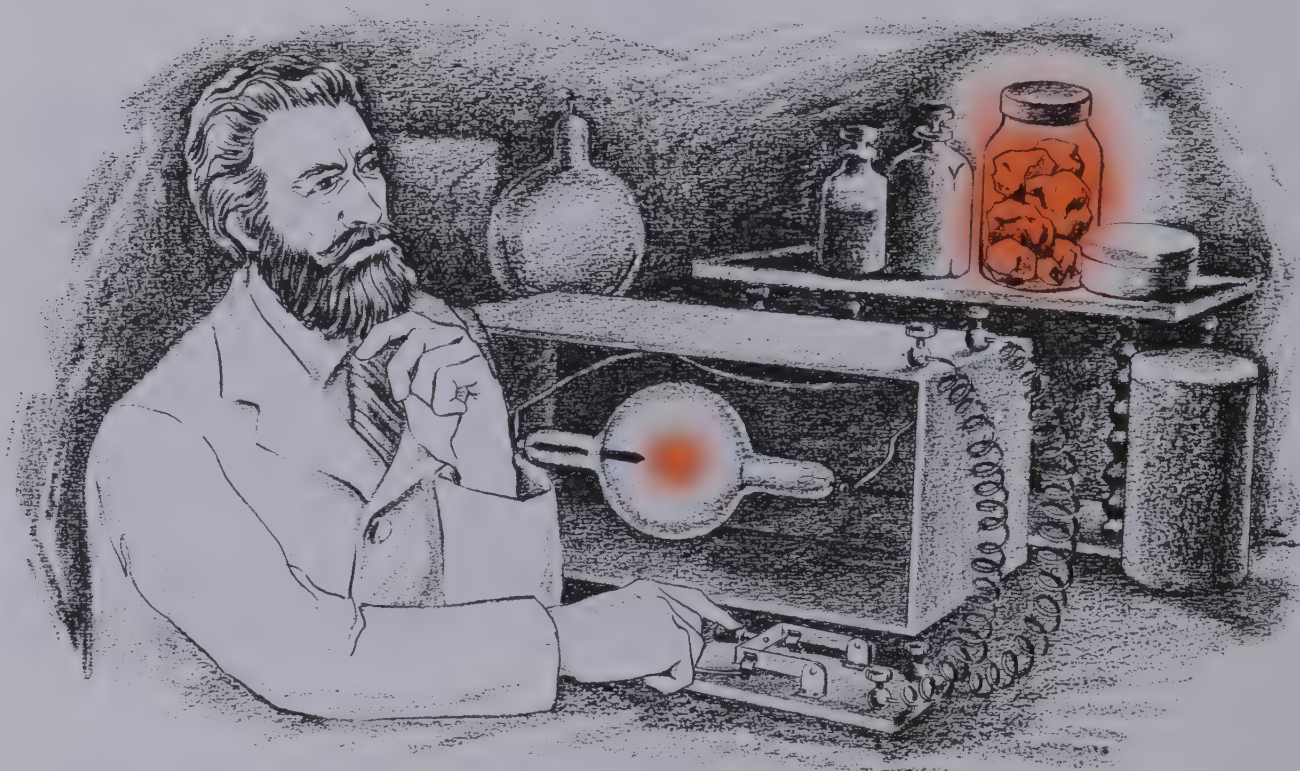
By 1910, just a century after the publication of Dalton's atomic theory, knowledge had progressed to the point where scientists no longer thought of the atom as a solid, but believed it to be an open, porous structure. The size of atoms had been roughly determined, but little was known about their internal structure. Within the next few years, a series of startling discoveries were made that explained many puzzling observations. Let's look at the story.

The Discovery of X-Rays

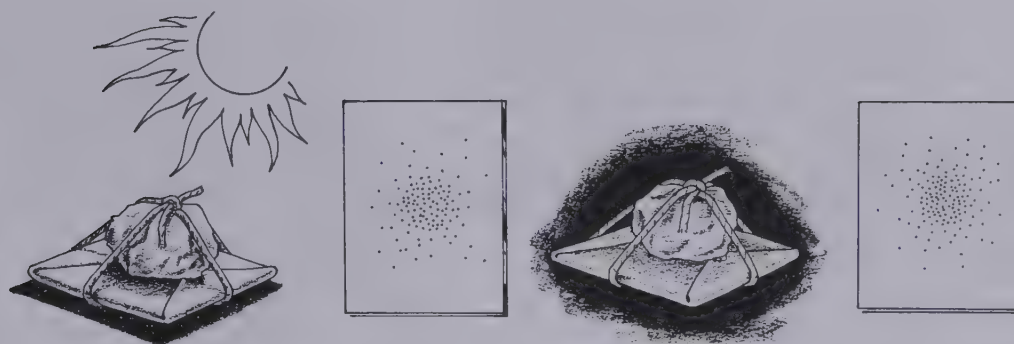
In 1895, Wilhelm Roentgen, a German scientist, was performing an experiment with a cathode-ray tube when he noticed that a bottle of fluorescent material on a shelf nearby was glowing. Even when he placed cardboard between the material and the cathode-ray tube, the glowing continued, but it stopped when he turned the tube off. This indicated that very penetrating rays were coming from the tube. Because of their mysterious nature, Roentgen called them x-rays. This turned out to be one of the most important discoveries of all time, because it provided a tool whereby the structure of the atom could be investigated.



An artist's depiction of the Thomson atom. Electrons oscillating back and forth in the positive globule could be thought of as producing the bulges depicted here.



Roentgen found that penetrating rays (x-rays) coming from a cathode-ray tube could travel through opaque substances and cause a nearby bottle of fluorescent material to glow.



Becquerel found that uranium was a source of rays that could pass through a heavily wrapped photographic plate and expose it. At first he thought this happened only when the uranium was exposed to sunlight (left), but he accidentally discovered it also happened in the dark (right).

Radioactivity

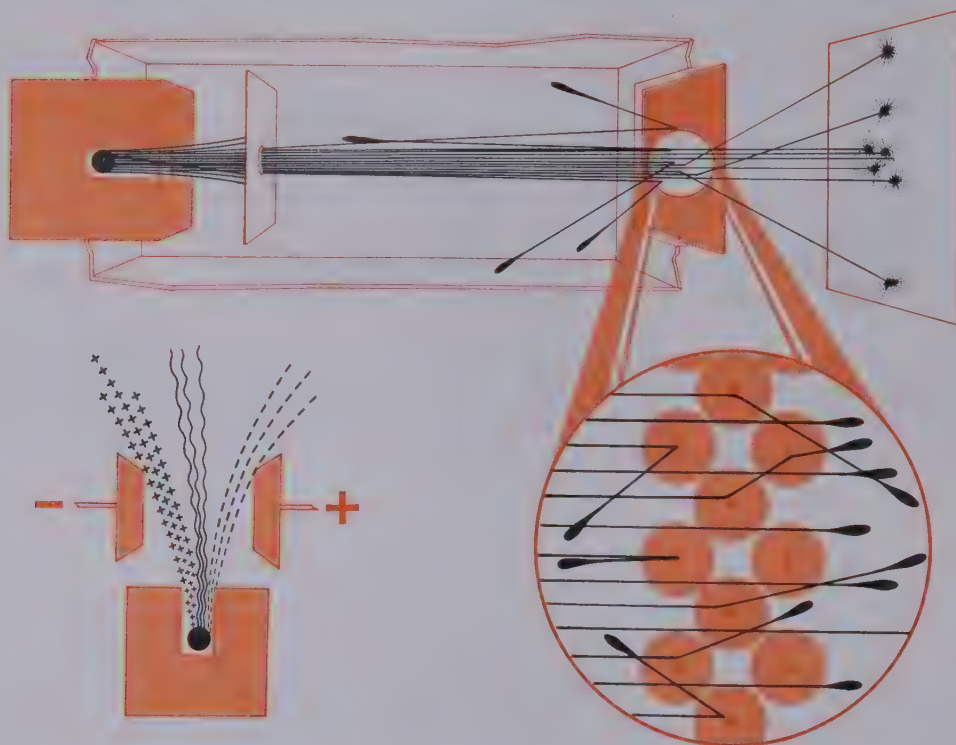
The following year, Henri Becquerel, a French chemist, was studying the nature of x-rays when he made a chance discovery. He had placed a photographic film in a drawer near a sample of uranium ore in preparation for an experiment. The film was ruined by the ore, but many controlled experiments had to be performed before the cause of the unexpected exposure of the film was determined. Finally, he found that the uranium ore spontaneously gave off penetrating rays which affected the photographic plate. This phenomenon is called *radioactivity*.

The three types of radiation emitted by naturally radioactive materials are alpha particles, beta particles, and gamma rays. It was soon learned that the alpha particle is the part of a helium atom which carries 2 units of positive charge and has a relative mass of 4 units. Because of its small size and its relatively large mass, the alpha particle proved to be a suitable tool for probing the internal structure of atoms.

Rutherford's Scattering Experiment

Ernest Rutherford (1871–1937), a New Zealand physicist, did extensive work on radioactivity and was awarded a Nobel Prize in 1908 for his contributions. He noticed that when a stream of alpha particles passed through a thin film of metal, the stream was broadened, or scattered, somewhat. He used alpha particles as “bullets” and directed them toward a piece of very thin gold foil. Most of the particles passed through the foil without being deflected and hit a fluorescent screen behind the foil. A fluorescent screen is a thick sheet of material which glows when it is struck by charged particles or other forms of radiation; the screen on a TV tube is an example of a fluorescent screen.

It was surprising that so many of the alpha particles easily passed through the gold foil, since Thomson's model predicted that the atoms would partly prevent particles from passing through.



Rutherford's apparatus. The enlargement (lower right) shows alpha particles bouncing off the nuclei in the center of atoms, according to the Rutherford model of the atom. The sketch at lower left shows that in passing by charged plates, alpha particles (+) move away from the positive plate toward the negative plate; gamma rays (wavy lines) move in a straight line; and electrons (−) move toward the positive plate.

But not all of the alpha particles passed the foil. Some bounced off to the side. A few even bounced straight back, as though they had hit something hard in the gold foil. This was very surprising, indeed: In Rutherford's own words, "It was quite the most incredible event that ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

Rutherford knew that it was impossible for an electron with its very small mass to make the heavy alpha particle bounce straight back. Since most of the alpha particles passed through the foil and a few bounced straight back, he reasoned that the gold atoms must be largely empty space, but contained a very tiny, extremely dense center which carried a positive charge. He called this dense, central core of the atom the *nucleus*.

The Discovery of Isotopes

In 1913, Frederick Soddy, a co-worker with Rutherford, and T. W. Richards of Harvard University discovered two different atomic weights for lead. Strangely, as frequently happens in science, they were working independently, using different methods and different lead sources. At about the same time,

Thomson discovered neon atoms which had differing weights. The name *isotopes* was given to atoms of the same element which have different atomic weights, but which have like chemical properties. Rutherford was able to explain the existence of isotopes on the basis of the very dense nucleus, thought to be the core of the atom. However, it was not until 1932 that the real explanation for isotopes was discovered. James Chadwick, a former student of Rutherford, demonstrated the presence of a neutral particle in the nucleus of atoms. This particle has the same mass as the proton but no charge. It is called a *neutron*.

5-8. THE RUTHERFORD MODEL OF THE ATOM

On the basis of these discoveries, Rutherford proposed a model for the atom which was vastly superior to any previous one. Its principal characteristics were:

1. The atom contains a very dense, positively charged nucleus.
2. The nucleus is surrounded by electrons which move in a comparatively large region of space about it.

This model gained almost immediate acceptance because it presented the concept of a positive nucleus which could account for radioactivity and atomic mass, and it pictured the electrons as being able to move about the nucleus, thus paving the way to an explanation of the chemical behavior of elements and of electricity.

However, Rutherford's model also raised some serious questions that could not be answered until more information became available. One question was that if the nucleus is positively charged and electrons are negatively charged, what kept the electrons from being attracted into the nucleus? Rutherford proposed that the atom was a small planetary system with electrons revolving about the nucleus much as the planets move about the sun in definite orbits. This turned out to be a poor model. We can explain the operation of a planetary system by the laws of mechanics because it is a gravitational system. The atom is an electrical system, and the same laws do not apply to both kinds of systems.

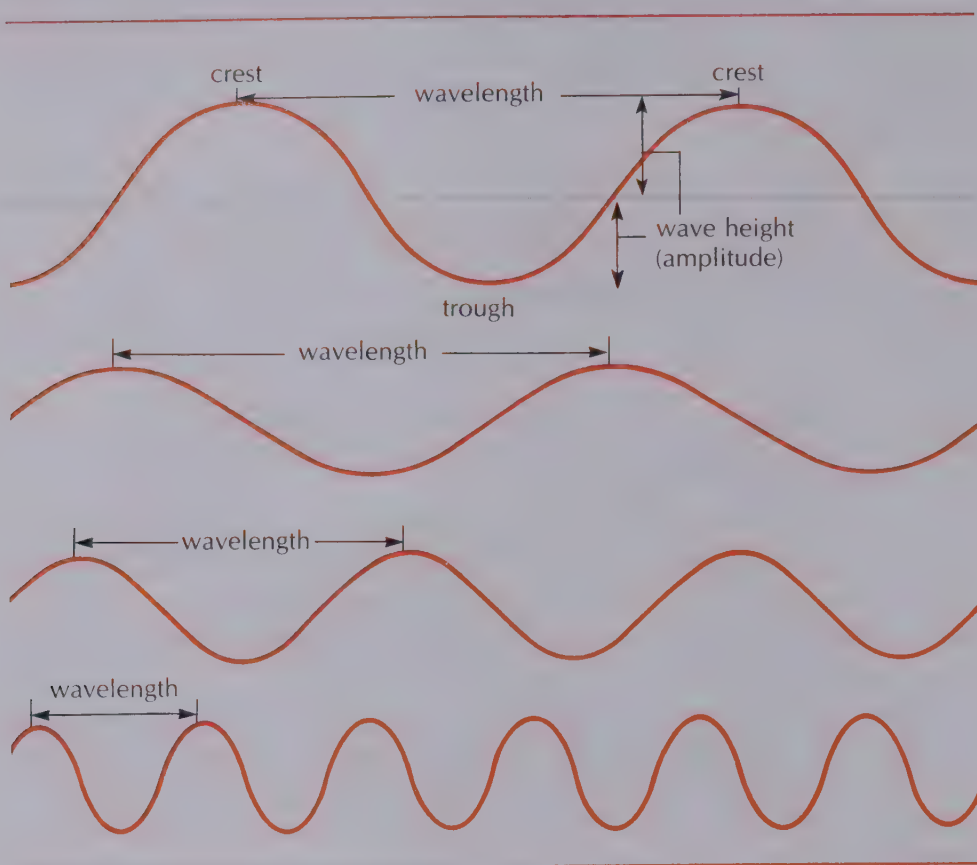
5-9. ELECTROMAGNETIC RADIATION

In order to understand the more recent developments in the atomic theory, it is necessary to know something about radiant energy. About 1600, scientists were trying to explain light. Isaac Newton and Christian Huygens, a Dutch astronomer, proposed conflicting ideas about the nature of light.

Huygens thought light was composed of waves, and Newton believed it consisted of a stream of tiny particles. According to Huygens, the motion of light waves is similar to water waves and sound waves. All wave motions have certain similarities, and we need to know some of the characteristics of waves if we are to appreciate the manner in which different kinds of energy are transmitted.

Characteristics of Waves

A wave is generally described in terms of two characteristics: wavelength and frequency. Let us examine the diagram of a wave to become familiar with its parts.



The *crest* is the highest part of a wave and the *trough* is the lowest point. The distance from the crest (or trough) of one wave to the next crest (or trough) is its *wavelength*. One half the difference between the crest and the trough is the height, more commonly called the *amplitude*. The number of crests (or troughs) that pass a certain point in one second is known as the *frequency*.

As you might guess, the longer the wavelength, the lower the frequency. If there is a large distance between crests, it takes more time for two successive crests to pass a point, and fewer crests will be counted per second. The shorter the wavelength, the higher the frequency. That is, if successive crests are close together, they require less time to pass a point, and more crests will be counted per second.

Radiant energy waves are different from sound and water waves because they can be transmitted through a vacuum, whereas sound and water waves can be transmitted only through a medium such as air or water.

Light and Electromagnetic Radiation

About 1860, James Clerk Maxwell, a young mathematical physicist from Edinburgh, Scotland, developed a model for light. His model suggested that

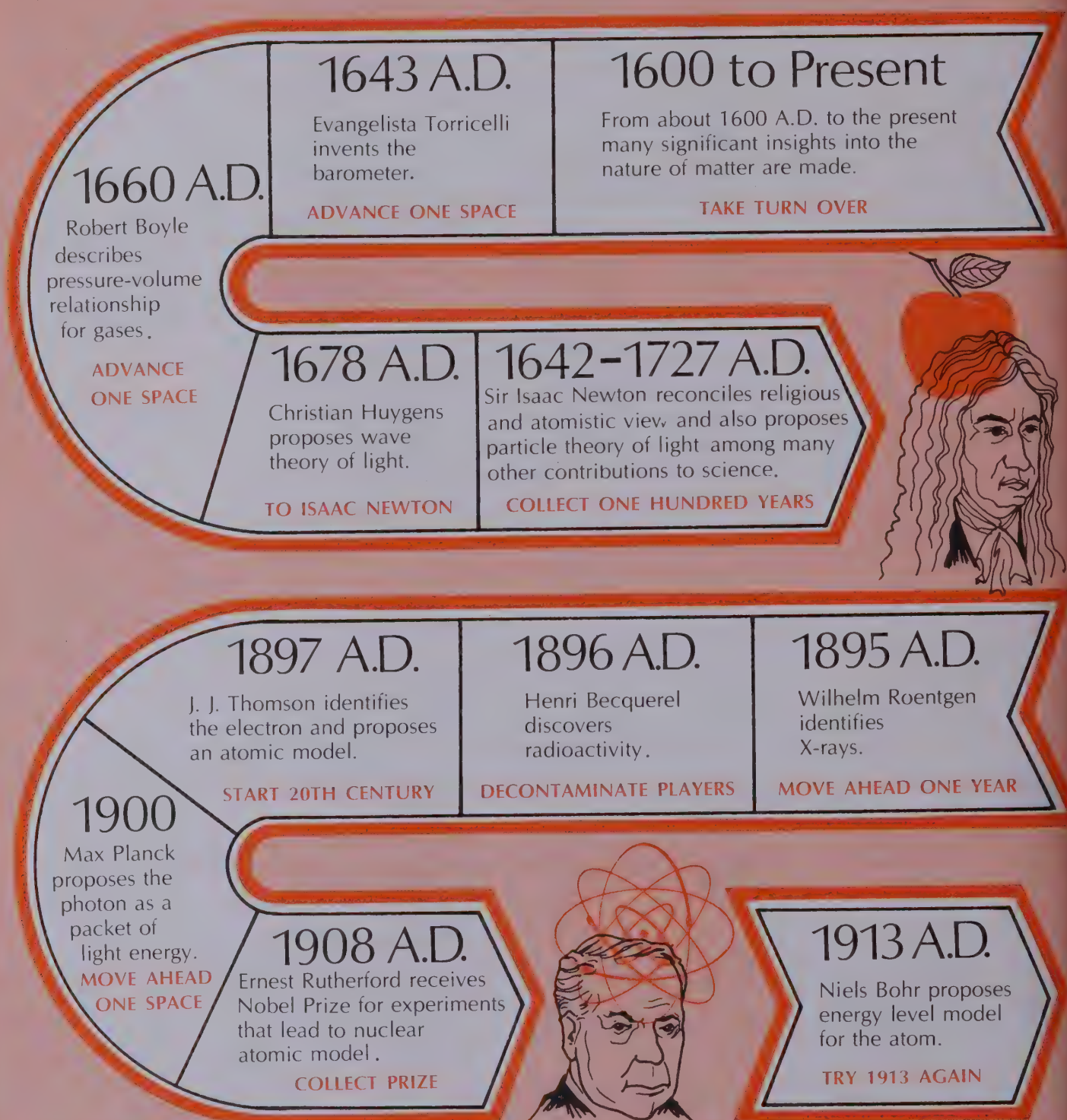
light is in the form of waves with both electrical and magnetic properties. He predicted the existence of electromagnetic waves with wavelengths too long for the eye to detect. His prediction was confirmed in 1888 when Heinrich Hertz, a German scientist, produced radio waves. These are electromagnetic waves, similar to light, but have a longer wavelength. Since 1888, several different types of electromagnetic radiation have been identified. These are summarized in Table 5-1.

Electromagnetic Radiation				
Type	Function	Source	How Detected	Wavelength Range in Meters
Radio, AM	communication	electrical circuits	electronic receivers	545 to 188
Radio, FM	communication	electrical circuits	electronic receivers	3.40 to 2.78
TV bands	communication	electrical circuits	electronic receivers	5.55 to 0.34
Infrared (heat)	special photography medicine drying paint	hot bodies	photo film thermocouples thermometers skin (nerves)	3×10^{-3} to 8×10^{-7} (0.003 to 0.0000008)
Visible light	perception of objects and color	electric arc hot bodies fluorescent screens	photo film eye photo cell	8×10^{-7} to 4×10^{-7}
Ultraviolet	special photography tanning skin medicine killing bacteria forgery detection manufacture of Vitamin D	the sun electric arc	photo film Geiger counter photo cell	4×10^{-7} to 10^{-9}
X-rays	medicine detecting flaws in metals crystal structure authenticity of old paintings	impact of electrons on certain targets	photo film Geiger counter ionization chamber	10^{-9} to 10^{-11}
Gamma rays	scientific research	cosmic rays nuclear reactions	photo film spark chambers superheated liquid hydrogen	10^{-10} and less

Table 5-1

Time Line Game of Atomic Theory Development

Start



450 B.C.

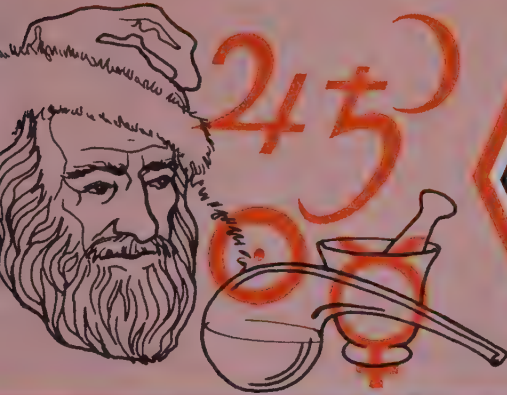
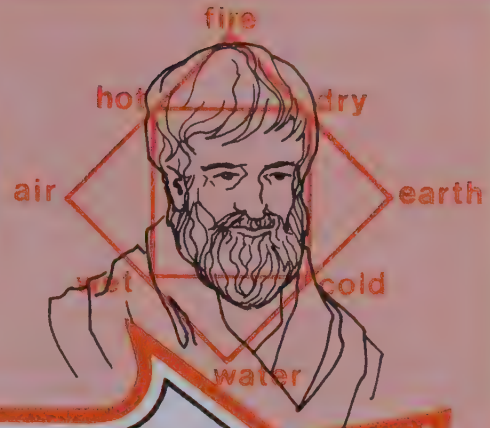
Democritus suggests atomic nature of matter.

ADVANCE 2 SPACES

384-322 B.C.

Aristotle rejects atomistic idea.

LOSE 1 TURN



300 B.C. to 1600 A.D.

Alchemists and artisans the world over are learning many things about matter and how to use it. Theories that explain nature of matter are proposed; none have the power and possibility needed.

ADVANCE TO 1600 A.D.

1790 A.D.

Jacques Charles describes the temperature-volume relationship for gases.

MOVE TO 19TH CENTURY

1808 A.D.

J. L. Gay-Lussac identifies the Law of Combining Volumes.

TAKE ANOTHER TURN

1808-1810

John Dalton publishes his New System of Chemical Philosophy in which he describes his atomic theory.

TAKE A BONUS TURN

1811

Amedeo Avogadro suggests that equal volumes of gases contain equal numbers of molecules.

ADVANCE ONE SPACE

1888 A.D.

Heinrich Hertz produces radio waves.

ADVANCE TO X-RAY

1860 A.D.

James Maxwell identifies light as having electric and magnetic properties.

MOVE AHEAD ONE SPACE



1913 A.D.

Frederick Soddy and T. W. Richards both discover isotopes of lead.

MOVE ONE SPACE

1932 A.D.

James Chadwick identifies the neutron.

ADVANCE TO PRESENT

Present

The wave mechanical model becomes the accepted model for the atom.

LOOK TO THE FUTURE

2000 A.D.

5-10 • NEW DISCOVERIES ABOUT THE NATURE OF LIGHT

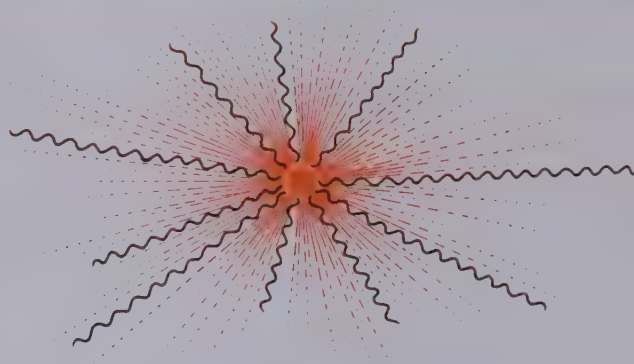
The controversy over the nature of light continued for about 200 years. In the late 19th century, it was generally concluded that the properties of light could be explained best by using the wave theory, and the matter was thought to be settled. The frequency of a light wave was thought to be related to the color of the light, with red light having the lowest frequency and violet the highest. However, the wave theory of light could not explain certain experimental observations, such as the color of radiation from heated objects.

For example, if you heat a metal rod and observe it in the dark, it will glow with a dull red color. If you heat it further, the glow becomes brighter and the color changes to orange-red. At still higher temperatures, the color of the glowing metal changes to white. At very high temperatures, the color is bluish-white. Although these facts had been known to men for centuries, no one had been able to think of an acceptable explanation for them.

In 1900, Max Planck, a German physicist, boldly proposed that radiation is emitted, not as waves, but in tiny packages. Each tiny package was assumed to contain a definite amount of energy, proportional to the frequency of the radiation. Each package was called a *quantum*.

Einstein carried Planck's theory a step further. He said that the quantum idea could be applied to radiation through a vacuum and also that radiation is absorbed one quantum at a time. We now call the quantum of radiant energy a *photon*.

Which theory is correct, the wave theory or the particle theory? All we can say at present is that the wave theory explains some of our experimental

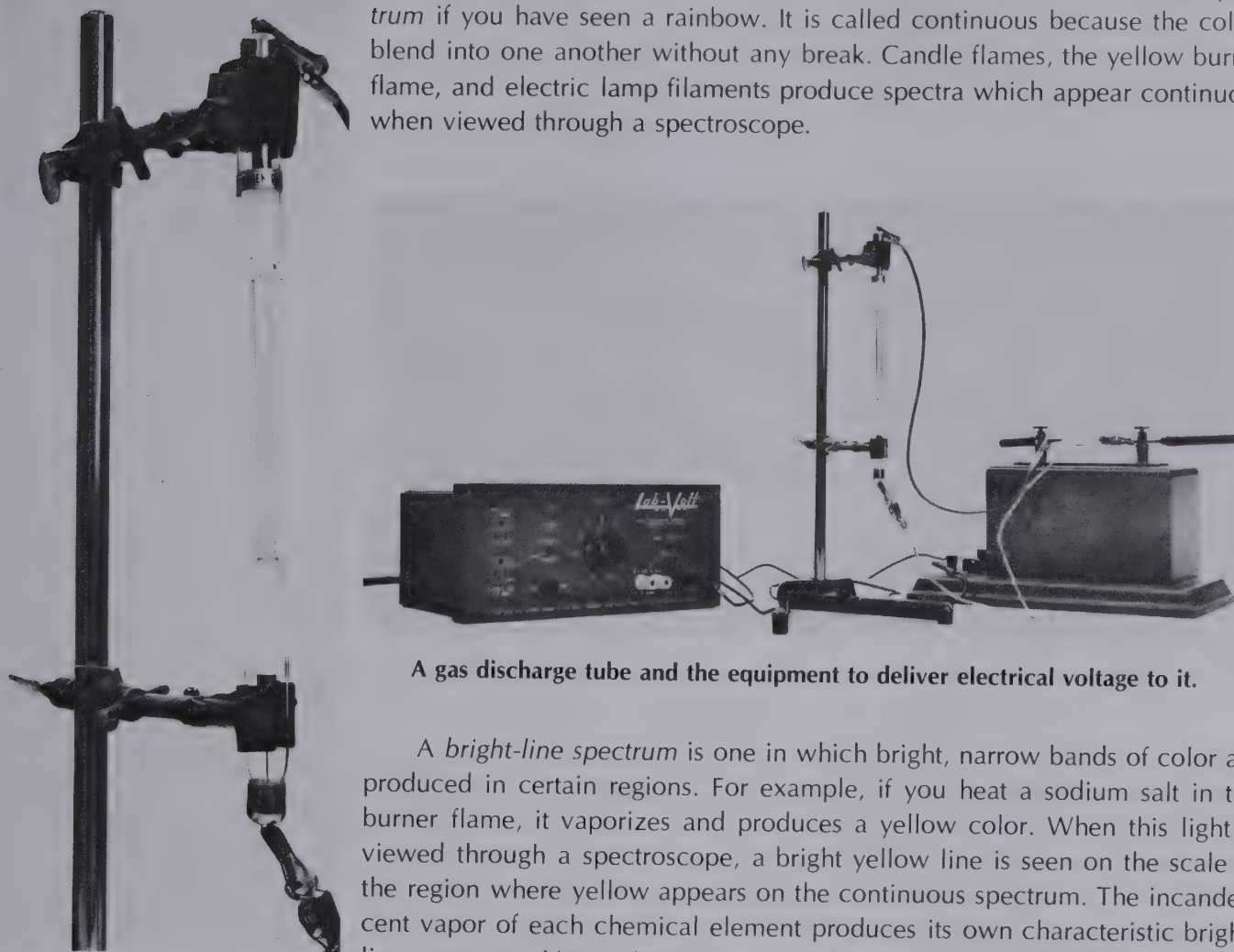


Is light made of waves or particles?

observations, but not all. The particle theory of light explains other observations. Neither theory is sufficient alone, so we use both of them. It should be noted that an experiment to illustrate the wave nature of light may be successful, and an experiment designed to illustrate the particle nature of light may be successful; however, one cannot demonstrate both characteristics in the same experiment. We can get answers from nature only by doing experiments, and nature will answer our questions only if we ask the proper questions in the proper way. This is not an easy task.

5-11 • ATOMIC SPECTRA

Much of the evidence for understanding the structure of atoms has come from the study of the spectra of elements. You are familiar with a *continuous spectrum* if you have seen a rainbow. It is called continuous because the colors blend into one another without any break. Candle flames, the yellow burner flame, and electric lamp filaments produce spectra which appear continuous when viewed through a spectroscope.



A gas discharge tube and the equipment to deliver electrical voltage to it.

A *bright-line spectrum* is one in which bright, narrow bands of color are produced in certain regions. For example, if you heat a sodium salt in the burner flame, it vaporizes and produces a yellow color. When this light is viewed through a spectroscope, a bright yellow line is seen on the scale in the region where yellow appears on the continuous spectrum. The incandescent vapor of each chemical element produces its own characteristic bright-line spectrum. Very minute amounts of elements can be identified in this manner. This is useful in crime detection and in analyzing the elements present in the nose cones of experimental rockets. The color of neon signs is the color of the glowing gas, neon, confined in a glass tube. Other colors of such signs come from other elements (or, sometimes, by using tinted glass tubing).

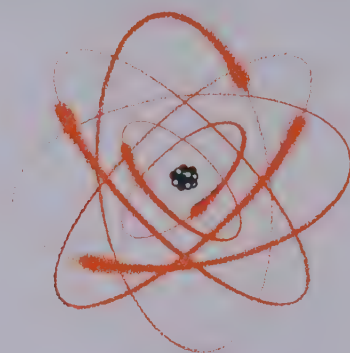
5-12 • THE BOHR MODEL OF THE ATOM

Niels Bohr was a Danish physicist who went to work in Rutherford's laboratory about the time the nuclear model for the atom was being proposed. As you will recall, one problem raised by Rutherford's nuclear atom was why the electrons did not fall into the nucleus. Another problem was why the spectra of elements appear as bright lines instead of being continuous. Bohr concluded that the models then used did not apply to atomic particles.

In 1913, using a new mathematical model, Bohr was able to calculate the frequencies of all of the then known lines in the bright-line spectrum of hydrogen, with one equation. Since hundreds of these lines were known, this

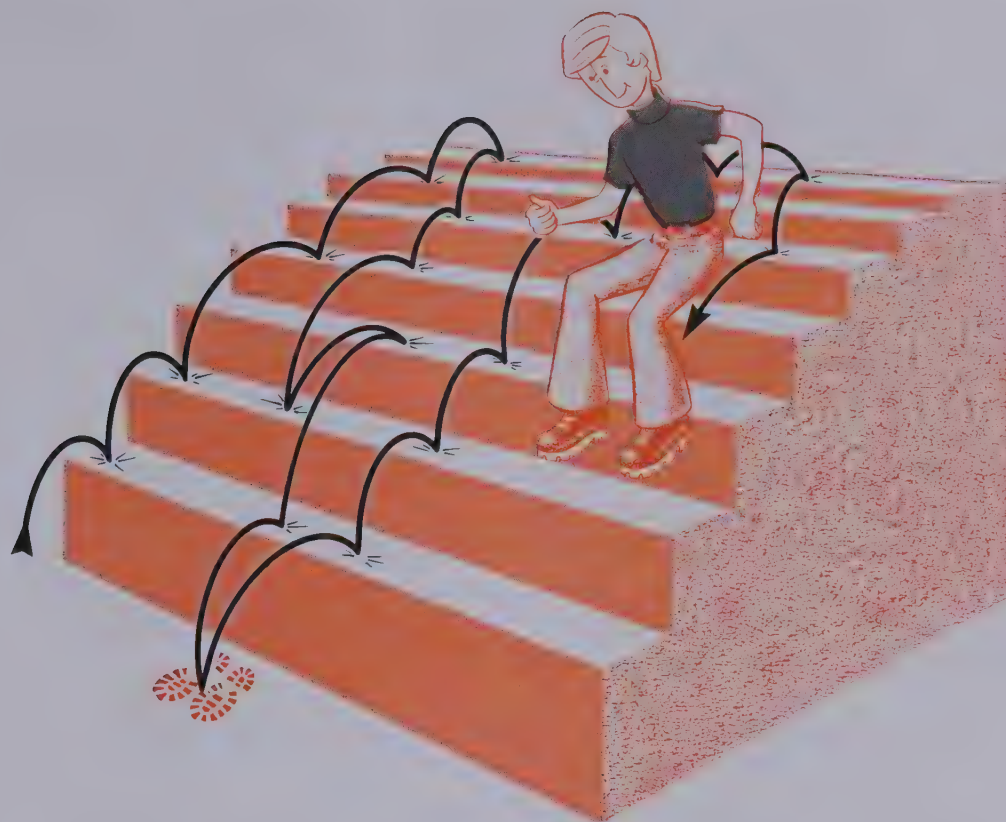
was a remarkable accomplishment. (Only when sophisticated research instruments are used, are these many lines detectable.) We can summarize Bohr's mathematical model as follows:

1. Electrons move in space about the nucleus only in certain specific energy levels.
2. So long as an electron remains within one energy level, it neither gains nor loses energy.
3. The stable energy levels specify energy of the electrons when they possess minimum energy; this condition is called the *ground state* of the atom.
4. When an atom absorbs a photon (quantum of energy), an electron jumps to a higher energy level. At this higher energy level the energy of the atom is greater; this condition is known as an *excited state* and is unstable.
5. When an electron moves back to any lower energy level, radiant energy is emitted as a photon of light of a specific frequency related to one of the lines in the spectrum of the element.
6. In another instance, when an electron is raised to a different, higher energy level and then moves back to a different, lower energy level, a photon of different frequency is emitted. That photon is related to a different line in the spectrum of the element.



The Bohr model of the atom.

If you think of Bohr's quantum jumps for the electron in terms of hopping up a staircase, it may be more meaningful. Let us assume you are going to move up a staircase by jumping on both feet from one step to the next. Obviously, you cannot stop between two successive steps; your two feet are either on the ground or else you exert sufficient energy to land on the first step. There is no stable position between steps. If you have sufficient energy to jump, step by step, all the way to step 7 and stop at that point, you now are in a state of high potential energy. You have done work in raising your body to this position. Your height above the floor is a measure of your potential energy. Now, if you jump down the steps one at a time, you will be losing potential energy. Suppose you jumped, for example, from step 7 to step 6, from 6 to 4 and from 4 to 1. If this descent could be viewed through a spectroscope, three different, sharp lines would be seen. This crude analogy may help



Analogous to energy levels and spectral lines, there are no stable positions between steps.

to make a very fundamental concept in modern atomic structure more understandable.

One fact must be stressed: the definite energy levels of the atom have no *physical* explanation; they are a *concept* invented by a scientist who had a thorough knowledge of physics and mathematics, plus a brilliant imagination. This is a good illustration of how a theory is born. A good theory explains what has been observed and enables us to predict what we have not yet observed. Bohr's theory did both of these quite well for a time. It explained the known spectrum of the hydrogen atom very satisfactorily and predicted the frequencies of the spectral lines for helium ions, for example. However, it failed to account for the spectra of many other elements. So, once again man was faced with the necessity to seek new facts, formulate new hypotheses, and develop new theories. The major contribution of the Bohr theory was the concept of "permitted" energy levels for the electrons. The more abstract model that followed, which we use today, employs this portion of Bohr's theory.

5-13. THE WAVE-MECHANICAL MODEL OF ATOMIC STRUCTURE

The latest theory for atomic structure is purely mathematical and represents a triumphant achievement of the human mind. It correlated centuries of separate and often unrelated experiments. We refer to it as the *wave-mechanical*

model. Knowledge of the calculus is necessary to its understanding. If you decide to pursue the study of chemistry, you will acquire the needed background and in due time will be able to follow the mathematical development of the wave equation. However, by using physical models you can employ the major concepts in the theory. This will enable you to think of the atom in a way which is sufficiently correct so that you can build upon the foundation at a later time if you so desire.

As you use these physical models to represent purely mathematical concepts, you must constantly be reminded that they are not exact in detail, but are crude representations of abstract ideas. You already use a similar approach in your use of a line and a dot in mathematics. By definition, a line has no dimensions except length; yet you do not hesitate to draw a line. And you know perfectly well that a line drawn with the sharpest pencil does have some width. In mathematics, a point is defined as a position in space with no physical dimensions: yet you consistently use a dot to represent a point. Even the smallest dot has some physical dimension. Likewise we use physical models in chemistry to represent concepts, but we do so with the full understanding that they are only aids to our comprehension.

5-14. ADVANTAGES OF THE HISTORICAL APPROACH TO ATOMIC STRUCTURE

We have taken time to present the development of the atomic theory of the structure of matter in its historical context for several reasons. Perhaps the most important reason is so that you can appreciate the nature of science as a human activity. You have been able to see how the work of one person provides a foundation upon which those who come after him may build. It is not of great consequence whether a theory advanced by one individual is "correct" or "incorrect." His major contribution is that he made observations and through the use of intelligent imagination proposed an explanation for his observations. Some scientists were able to take great intuitive leaps and make bold and daring assumptions. These provided clues and furnished ideas to stimulate the creative powers of individuals who came on the scene later.

A second reason why we have approached atomic structure from the historical standpoint is to show the interdependence of fact and theory. Facts are useful because they stimulate the development of theory. In turn, a theory is of value only when it explains existing facts. We have seen that as new facts are discovered, theories must be modified to accommodate them. Likewise, modification of a theory results in a better understanding of facts. Each is dependent upon the other.

The third reason for this approach is to emphasize the role of each individual contribution in the development of science. The major advances in the development of the atomic theory have been the result of personal effort and imagination. But any theory becomes valuable only when it is tested by the scientific community. Theories which cannot be tested objectively are of questionable value to science.

With this background, we will study the structure of individual elements and seek to establish a pattern for their classification.

Practice Exercises *(Answers on p. 313)*

1. What is meant by a “black box” as we use the term in science?
2. Discuss three ways in which the work of Dalton influenced the advancement of science.
3. How did the discovery of sub-atomic particles partially destroy the Dalton model of the atom?
4. Describe the Rutherford model of the atom and state at least two questions it failed to answer.
5. State the major contribution to science made by: (a) Richards and Soddy, (b) Planck, (c) Avogadro, (d) Millikan, (e) Democritus.
6. State the flame color associated with these ions: (a) Sr^{2+} , (b) Cu^{2+} , (c) Na^+ .
7. State the color of the borax bead associated with these ions: (a) Ni^{2+} , (b) Co^{2+} , (c) Mn^{2+} .
8. Describe a wave and explain how radiant energy waves differ from sound waves.
9. How did Dalton explain the existence of the compounds NO and NO_2 ?
10. Summarize the biography of one scientist who contributed to the development of atomic theory.
11. (Multiple Completion; see special directions in Appendix 13)
Bohr’s model of the atom included these assumptions:
 1. Electrons move in the atom only in certain specific energy levels.
 2. So long as electrons remain in a given energy level, they neither gain nor lose energy.
 3. When electrons move to a lower energy level, they emit light of a specific frequency.
 4. In the ground state of the atom a condition of maximum energy exists.

Self-Test *(Answers on pp. 313, 314)*

1. Name one “black box” that scientists are working with today and state your reason for listing it as a “black box.”
2. Cite specific examples to show that Dalton had a good imagination.
3. What major discovery destroyed the Thomson model of the atom?
4. State the major contribution to science made by: (a) Dalton, (b) Thomson, (c) Becquerel, (d) Bohr, (e) Rutherford.
5. Discuss three reasons for studying the development of the atomic theory in historical context.
6. State the flame color associated with these ions: (a) Ca^{2+} , (b) K^+ , (c) Ba^{2+} .
7. State the color of the borax bead associated with these ions: (a) Cr^{2+} , (b) Co^{2+} , (c) Ni^{2+} .
8. Draw and label a wave and explain how radiant energy waves are different from water waves.
9. Explain how the compounds CO and CO_2 illustrate the Law of Multiple Proportions.
10. Describe the experiment that led Rutherford to propose the nuclear model for the atom.

11. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION

Thomson believed that cathode rays were composed of matter

REASON

Because both electric and magnetic fields caused the rays to be bent.

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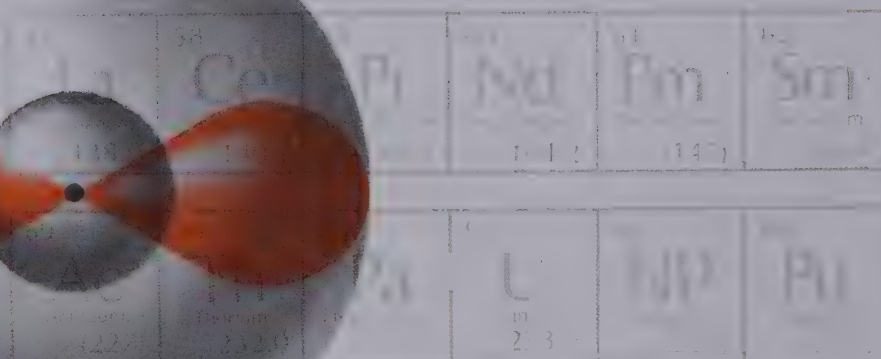
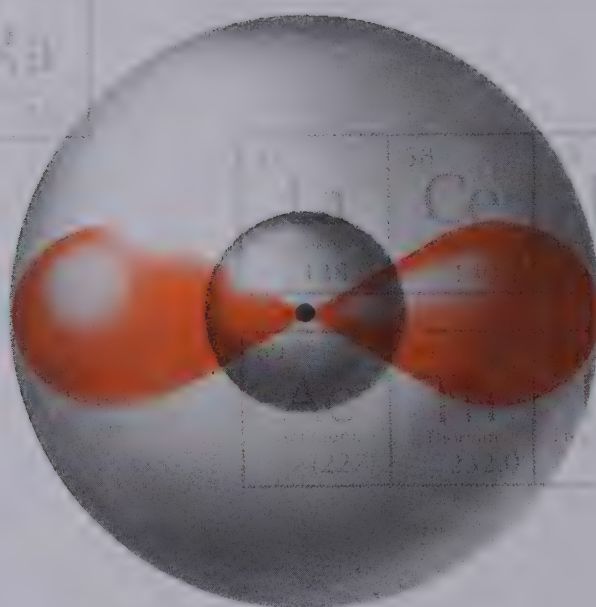
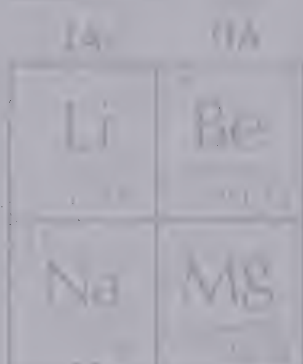
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From Boyle to Bohr, nine scientists explain their work and major achievements in the development of chemistry. Paperback.





THE ELECTRONIC STRUCTURE OF ATOMS AND THE PERIODIC LAW

OBJECTIVES:

By the time you have completed your study of Chapter 6, you will be expected to demonstrate acceptable performance on the following objectives.

1. Compare the size of atoms relative to the size of their nuclei.
2. State the relative mass of the electron, the proton, and the neutron.
3. Define atomic number and discuss the significance of atomic number in determining the properties of the elements.
4. State the major contributions of Moseley and Mendeleev to the development of chemistry.
5. Describe the position of the electron in relation to the nucleus, using an analogy or model to illustrate.
6. Write the electron configuration for any element, given the atomic number.
7. Write the orbital notation for any element, given the symbol and the atomic number.
8. Write the electron dot notation for any element, given the symbol and the atomic number.
9. State and explain the following trends:
 - a. The effect of increasing atomic number on atomic radius.
 - b. The effect of increasing atomic number on ionization energy.
10. Define: chemical family, period, series, group, transition element, lanthanide series, actinide series.
11. Summarize the major advantages of the periodic table.
12. Identify three weaknesses of the periodic table.
13. Using a blank chart which represents the periodic table, predict the following, given the family or period of a series of elements:
 - a. Whether atomic size is increasing or decreasing with increasing atomic number.
 - b. Whether ionization energy is increasing or decreasing with increasing atomic number.
 - c. The expected number of electrons in the outer energy level.
 - d. Whether *s*, *p*, *d* and/or *f* orbitals are filled or partly filled.
 - e. The expected electron configuration of an element.
14. Identify the following cations by the appropriate laboratory method: Ag^+ , Pb^{2+} , Sb^{2+} , Bi^{2+} , Cu^{2+} , Hg^{2+} , and Hg_2^{2+} .

SUGGESTED ORDER OF STUDY

1. Study Secs. 6-1 through 6-4.
2. Perform Exps. 6-1 through 6-4. ✓

Note: These must be done in class and each one must be approved by the instructor prior to advancing to the next one.

3. Perform Exp. 6-5. ✓
4. Study Secs. 6-5 through 6-7.
5. Perform Exp. 6-6. ✓
6. Study Sec. 6-8 and read bibliographical references.
7. Do the Practice Exercises; review.
8. Take the Self-Test and review as needed.
9. Take test on Chapter 6.

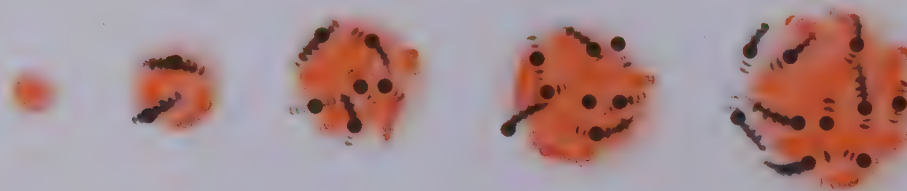
6-1 • THE ATOMIC NUCLEUS

We have studied the cumulative evidence for the present concept of the atom. The atom seems to have a dense, positively charged, central core—the nucleus. Swarming about the nucleus with various amounts of energy are the electrons. In this chapter we will learn how electrons are described according to their probable location in the atom and, through knowledge of atomic structure, will arrive at a system of classification, or grouping, which greatly simplifies the study of chemistry. Not only does grouping enable us to study the properties of the elements more effectively, but it also allows us to predict the properties of their compounds.

The average diameter of the nucleus is about 10^{-13} cm, although this varies somewhat from element to element. The average diameter of an atom is about 10^{-8} cm, or roughly 100,000 times that of the nucleus. This indicates that the atom is mostly empty space!

Many particles are believed to exist in the nucleus, but at this time we are concerned with only two: the proton and the neutron. *Protons are positively charged particles* with an actual mass of about 10^{-24} gram, which is about the same as the mass of a hydrogen atom. In 1912, H. G. J. Moseley, an English physicist, stimulated the development of a theory that the number of protons in the nucleus determines the properties of an element. The number of protons in an atom is called the *atomic number*. If the theory is correct, since no two elements have atoms with the same atomic number, this provides a reliable method for identifying an element. For example, hydrogen has 1 proton in its nucleus. No other element has just one proton. Oxygen atoms have 8 protons and the element with atomic number 103, Lawrencium, has 103 protons in the nucleus of each of its atoms.

The neutron is a nuclear particle with no electrical charge. It has about the same actual mass as the proton and a relative mass of 1. Therefore, neutrons contribute to the mass of an atom, but have no effect upon the charge. Since protons and neutrons are both contained within the nucleus, most of the mass



A depiction of the nuclei of several atoms.

of an atom is concentrated in this central core. The number of neutrons in a nucleus can vary from atom to atom of the same element. This variation in atomic mass caused by the presence of neutrons explains the existence of isotopes. The most common isotope of hydrogen contains no neutrons. A less common isotope of hydrogen contains one neutron, and a rare isotope contains two neutrons. Neutrons do not appreciably affect the chemical properties of an element.

We normally expect *like* electrical charges to repel each other. You may wonder how protons, each carrying a single positive charge, can exist so close to each other in the nucleus of an atom. Investigate this problem by reading more about the nucleus.

6-2. ELECTRONS AND ORBITALS

Electrons are negatively charged particles with an actual mass of about 10^{-27} gram and a relative mass of zero. All electrons are identical, regardless of where they are found. The number of electrons in any neutral atom is equal to the atomic number of that element. Hence, an atom is neutral when it contains equal numbers of electrons and protons.

In the rest of this chapter we shall be concerned with these electrons. Our task is to learn some of the ways used to describe these very tiny particles, which no one has ever seen. They may not even exist! That is, scientists have only developed a model called the wave-mechanical model of the atom which, if true, gives us some idea of what electrons are like and what they do as they scoot about here and there near the nucleus of an atom.

According to this model, it is best to think of the electrons as being somewhere near the nucleus but not in any particular place at a given time. Instead of saying exactly where an electron might be found right now, it is possible to say only that it is probably located somewhere in a region of space that is no more than about 10^{-8} cm in diameter. Some of these regions are probably spherical. Some of them are probably shaped like two pears placed end to end. Some of the electrons in an atom with more electrons are probably located in regions of space shaped like four and six pears placed with their small ends together, and in an atom with many, many electrons, some are probably located in still other regions of space with different shapes.



These regions of space are called *orbitals*. There are *s* orbitals (you can think of *s* as spherical). There are *p* orbitals (think of this as the two pears end to end). There are *d* orbitals (you can think of a doubled *p*, four pears). There are *f* orbitals (fancy shaped regions). There are *g* (gosh, look at that shape) orbitals; *h* (holy cow, what a shape) orbitals; *i* orbitals (I never would have thought of a region with that sort of shape), and so on:

s, p, d, f, g, h, i, j, k, etc.

It is helpful to remember the letters for the differently shaped orbitals in this order. After the first three, *s, p*, and *d*, beginning with *f* the order is alphabetical; and for us this alphabet has only about eight or nine letters, up to *j* or *k* or so.

So, according to the model, an atom has electrons buzzing around the nucleus, something like a swarm of bees buzzing around a beehive. The difference is that if we were brave enough to risk getting stung, we could say where a certain bee is at a certain instant, but this is not possible for electrons. Instead, for electrons, we can say only probably where one of them is when it is buzzing about its nucleus. We can say that it is in a fairly small spherically shaped region, a *1s* orbital, or in a larger spherically shaped region, a *2s* orbital, or in a still larger spherically shaped region, *3s*; or *4s*, and so on. The



numbers, 1, 2, 3, and so on, that are helpful in giving us an idea about the comparative size of the orbital, are called *principal quantum numbers*. You remember the word *quantum* from Chapter 5. The wave-mechanical model of the atom was developed from the quantum theory which Max Planck had devised, and combined with other models, plus some new ideas as well.

As you may have guessed by now, there are different sizes of *p* orbitals; a *3p* orbital is smaller than a *6p* orbital, for example. But, for *p* orbitals, a *2p* orbital is the smallest. There is no *1p* orbital; a handy way to remember this is to recall that *p* is the *second* letter in this atomic alphabet: *s, p, d, f*, etc. So, you can now guess correctly that of all the different *d* orbitals, the *3d* is the smallest; for *f* orbitals, we have *4f* as the smallest, then *5f* a bit larger, *6f* still larger, and so on.

6-3. ELECTRON CONFIGURATIONS

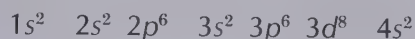
Perhaps a picture of the atom is beginning to develop in your mind by this time. Suppose we have an atom with only one electron. This would be the hydrogen atom, of course, since it has only one proton in its nucleus. The

negatively charged electron would tend to get as close as possible to the positively charged nucleus. The electron would be in the $1s$ orbital.

It is desirable to describe all of the electrons in an atom, as you will see later in this chapter. If you are asked to describe the lone electron in a hydrogen atom, you would say " $1s^1$." The extra 1 above the s on the right indicates one electron in the $1s$ orbital. A helium atom has two electrons. What is the electron configuration of helium in the ground state? Answer: $1s^2$.

Our question is the sophisticated way to ask for a description of the probable locations in space of the electrons in an atom, those locations in which the electrons have the least energy. Ground state is another way of referring to the state of lowest energy. That is, an orbital is a region in space where an electron is probably located, as we know. It is also a description of the energy state. A $5s$ orbital represents a great deal more energy than a $1s$ orbital; an electron in a $2p$ orbital has less energy than an electron in a $3p$ orbital. An electron in a $2s$ orbital has a different energy than an electron in a $2p$ orbital, but not much different, at least not enough different to bother us. We can say that electrons in $2s$ and in $2p$ orbitals are in the same energy level. Similarly, $3s$, $3p$, and $3d$ orbitals can be thought of as the same energy level.

Orbitals with different shapes—different letters such as s , p , d , f , and so on—each have different energies associated with them. The principal quantum numbers also signify different energies when we use them with the letters. We can expect an atom with many electrons to have electrons in several different orbitals, each with a different energy. For example, the electron configuration of a nickel atom in the ground state is:



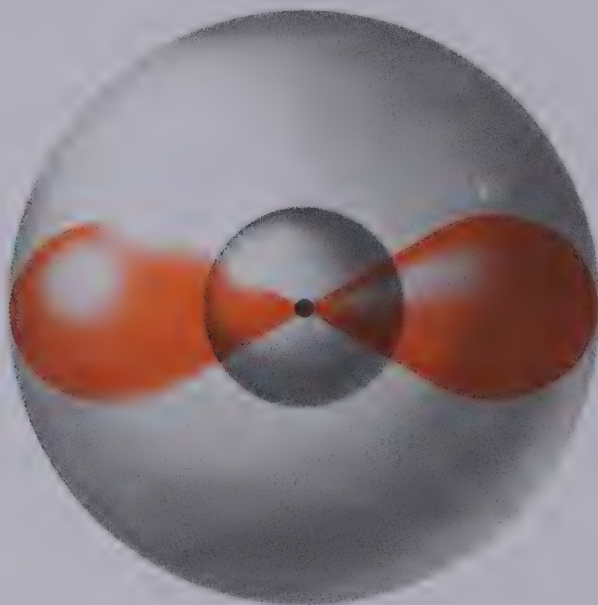
This electron configuration tells us in a qualitative way the shapes of the regions where it is probable that we would find the twenty-eight electrons, and it tells us the energies of the electrons. If we used the fancy mathematics that is also part of the wave-mechanical model of the atom, we could apply the electron configuration of nickel to tell us the quantitative details of probable location and energy.

Let us continue; we have ground state electron configurations of hydrogen, with one electron, $1s^1$, and helium with two electrons, $1s^2$. Next is lithium with three electrons. The ground state electron configuration of lithium is $1s^2 \ 2s^1$. You would think offhand that there would be three electrons in the $1s$ orbital for lithium unless you remember that electrons all have a negative charge and repel each other, something like two brothers in the same family. Although they are willing to share the same room (sometimes), they also sometimes find each other repulsive. In a way, it is the same with electrons; they do repel each other, and only two electrons can share the same orbital. If a third electron comes along, it has to occupy a different orbital. For lithium, the next lowest energy orbital after the $1s$ orbital is the $2s$ orbital. Therefore, the ground state electron configuration of lithium is $1s^2 \ 2s^1$.

Beryllium has four electrons; its ground state electron configuration is $1s^2 \ 2s^2$. What about boron, with an atomic number of five? Since the $1s$ orbital

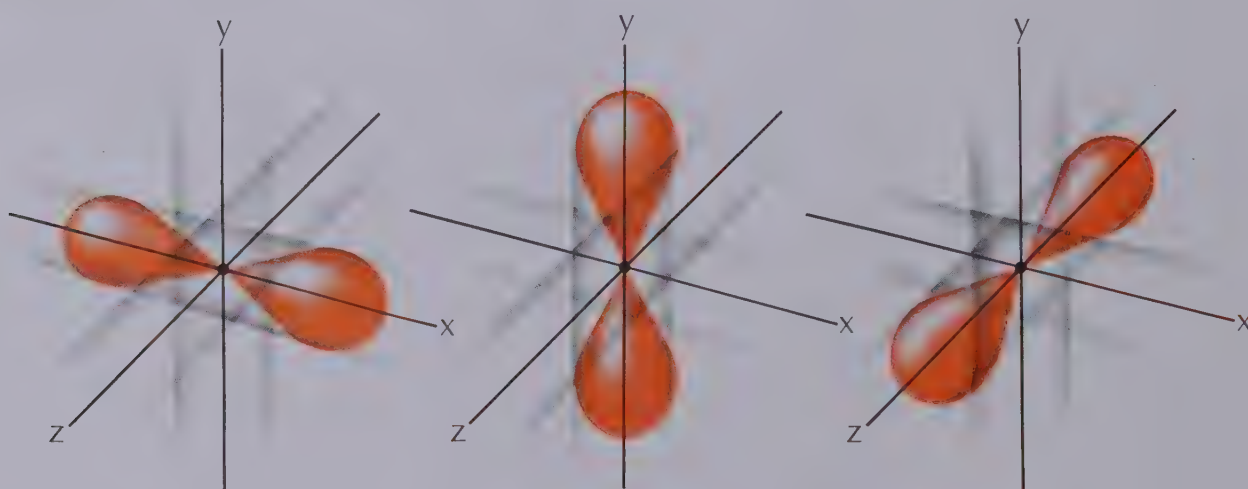
is filled with two electrons and the $2s$ orbital is filled with two more, the fifth electron goes into the $2p$ orbital. The electron configuration of boron is $1s^2 2s^2 2p^1$. (From now on, we will assume that each atom is in its ground state.)

Let us examine an artist's sketch of the wave-mechanical model for boron and its five electrons.



In the center, the tiny dot represents the nucleus. You can see the $1s$ orbital, the smaller of the two spheres, and the $2s$ orbital, which is the larger sphere. The $2p$ orbital is the shape that looks like two pears end to end. This $2p$ orbital has one electron in it somewhere. Notice that this $2p$ orbital has been drawn across the page, horizontally. The artist could just as well have drawn it vertically, or straight in and out of the page, if she had chosen to do so.

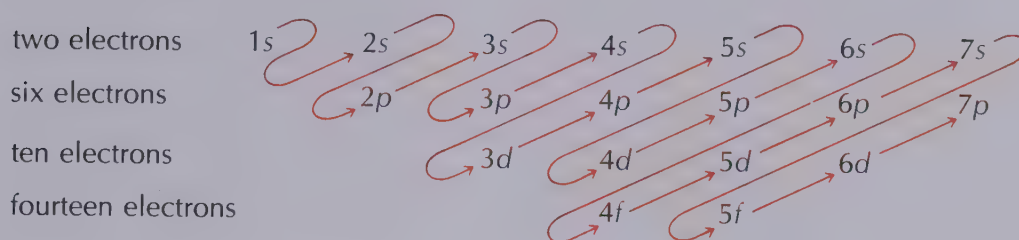
There are three different directions we could put the $2p$ orbital in, equally well. In the wave-mechanical model this is interpreted to mean that actually there are three $2p$ orbitals.



We cannot tell which of the three $2p$ orbitals the fifth electron in boron is occupying.

What is the electron configuration of oxygen, with eight electrons? Remember that there are three $2p$ orbitals, and each can have up to two electrons. The electron configuration of oxygen is $1s^2 2s^2 2p^4$. In neon, which has ten electrons, the $2p$ orbitals are completely filled; the electron configuration is $1s^2 2s^2 2p^6$.

After the three $2p$ orbitals are filled, with six electrons, the next lowest energy orbital is $3s$. Then $3p$ is next, and $4s$ is after that. Then comes $3d$. As you can see, this is beginning to get a little complicated. From lowest energy upward, the order is $1s$, with two electrons; $2s$ with two; $2p$ with six; $3s$ with two; $3p$ with six; $4s$ with two; $3d$ with ten (there are actually five equivalent $3d$ orbitals); $4p$ with six electrons; and on and on. The diagram shows a good way to keep all this in mind; you can make this diagram from memory any time you need it.



To use this diagram, start with the arrow on the upper left and check off " $1s$ "; then follow the dotted line to the next arrow, and for the second arrow check off " $2s$." Follow the next dotted line to the third arrow, and for the third arrow check off " $2p$ " and " $3s$ ", and so on. Refer again to the electron configuration for nickel; this diagram is how we figured it out. Notice that the total of all the superscripts in the electron configuration for nickel equals twenty-eight. This is the total number of electrons in an atom of nickel. The atomic number of nickel is twenty-eight; it has twenty-eight protons in its nucleus. Remember that in an atom the number of electrons outside the nucleus is the same as the number of protons inside the nucleus.

Problem:

Write the electron configurations for these elements: carbon, sulfur, silver, and mercury.

6-4. OTHER METHODS OF REPRESENTING ELECTRONS IN ORBITALS

Orbital Notation

Another method for representing the electron arrangement in atoms is known as orbital notation. In this method the orbital is represented by a small circle, \bigcirc . If only one electron is present, we designate it thus: \uparrow ; if two electrons

are present, the pair is represented in this manner: $\uparrow\downarrow$. An empty circle indicates an unoccupied orbital: \circ .

Example: Orbital notation for nitrogen, atomic number 7

Symbol	Orbitals		
	1s	2s	2p
${}_7\text{N}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$

Note that electrons do not form pairs in the p orbitals until each of the three p orbitals has one electron in it. For example, here are the orbital notations for boron, carbon, nitrogen, oxygen, and fluorine, each with one more electron than the preceding element.

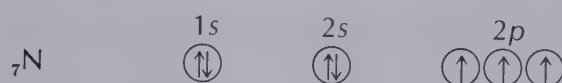
Symbols	Orbitals		
	1s	2s	2p
${}_5\text{B}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\circ\circ$
${}_6\text{C}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow\circ$
${}_7\text{N}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$
${}_8\text{O}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow$
${}_9\text{F}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$

According to the wave-mechanical model, it is possible to say that electrons have spin, as though they were spinning either clockwise or counterclockwise. To represent these two different spins, arrows pointing up and down are often used. We said that two electrons are the most that could occupy one orbital because they were repulsive to each other; this was our two-brothers model. The wave-mechanical model asserts that two electrons in an orbital cannot have the same spin. Since there are only two ways for an electron to spin, two electrons are the most that an orbital can hold. A third electron would be bound to have the same spin as one of the electrons already present. In the wave-mechanical model, this is called the *Pauli Exclusion Principle*, and in other books you will find other ways of stating this principle. The real statement of this principle is mathematical; it cannot be stated correctly in any other language.

Also, in other books you can learn about other quantum numbers. There are four: the principal quantum number, the orbital quantum number, the magnetic quantum number, and the spin quantum number. We have introduced you to this subject in this chapter, and nothing has been taught that is known to be incorrect, but we have left out a great deal of information. In learning about electrons in atoms, it is best to begin carefully. Actually, of course, you have learned much already. Let us apply this knowledge further:

Electron Dot Notation

Once you know how to draw electron configurations as orbital notations, it is possible to draw electron dot notations for the elements. This is very useful when we study bonding between two or more elements, as we will do in later chapters. In this method we use the symbol of the element and the electrons in the *outermost* energy level only. These are the electrons with the highest principal quantum number. For example, how do you draw the electron dot notation for nitrogen? Begin with the orbital notation:



Next, pay attention only to the electrons in the *outermost* energy level. These are the electrons in the orbitals with the highest principal quantum number, 2. There are two electrons, paired, in the 2s orbital. There are three more, each alone, in the three 2p orbitals. The pair of 2s electrons are shown as two dots close together and the three lone electrons are shown as three dots, separate from the others:



We have shown the pair of electrons on top of the symbol, N. This is unimportant; they could be shown on the bottom or on either side.

Problems:

1. Draw the orbital notations for hydrogen, neon, magnesium, and cobalt.
2. Draw the electron dot notations for hydrogen, sulfur, sodium, and neon.

6-5. REGULARITIES IN ELECTRON CONFIGURATIONS OF THE ELEMENTS

When you examine the electron configuration for the elements written in order of their *increasing* atomic number, some striking patterns emerge:

1. It becomes apparent that the orbitals fill in a systematic manner.
2. An outermost energy level never contains more than eight electrons.
3. The 4s orbitals fill before the 3d, indicating that they are lower energy orbitals. (Actually, this is not quite correct for some of the elements, but if we say this fully and correctly to describe the lower and higher of the 4s and 3d orbitals for each element, it gets to be more complicated than it really should, so we will let this go.)
4. At regular intervals, an energy level attains its maximum number of electrons.
5. At regular intervals, the next higher energy level begins to fill.

What does this mean in regard to properties of the elements? Before attempting to answer this question, let us look at the relationship between atomic number and atomic size.

Atomic Number and Atomic Radius

If you plot the atomic radii of the elements in order of increasing atomic number, you again observe a systematic pattern. At regular intervals, there is a sharp rise in the graph, followed by a more or less gradual decline, indicating a close relationship between the filling of the energy levels and the size of the atom. Do these patterns provide a clue to the properties of the elements? Let us examine another relationship in an attempt to obtain further evidence on which to formulate an answer to our question.

Atomic Number and Ionization Energy

We have been considering atoms in their ground state, or state of lowest energy. Chemists know that if sufficient energy is provided in the form of heat, light, or electricity, electrons can move from their normal position to higher energy levels. When this happens, we speak of the atom as being "excited." It is possible to provide enough energy to remove the most loosely held electron entirely. This leaves the atom with a net positive charge, since the number of protons and the number of electrons are no longer equal. Such charged atoms are called *ions*, and the energy required to remove the outermost electron is known as *ionization energy*.

If you plot the ionization energy for elements in order of increasing atomic number, a fairly definite pattern is again found to exist. The energy shows a gradual increase until a high point is reached. After each peak, there is a sharp drop, indicating that the two elements have greatly different ionization energies. There must be an explanation for these recurrent patterns.

6-6. CHEMICAL FAMILIES

In tabulating the results of your electron configurations, the graph of atomic radii, and the graph of ionization energy, all based upon arranging the elements in order of increasing atomic number, you found the same elements listed again and again. The fact that electrons in a given atom occupy definite energy levels and the fact that these levels fill in a definite order accounts for the patterns you obtained in plotting the graphs. Elements with similar electron configurations in the outermost energy levels are found to exhibit similar chemical and physical properties. Such elements are called *chemical families*. Let us examine the families you discovered as a result of your laboratory activities. We will summarize the families by comparing electron configurations and will list a few more important properties to see how these vary from one member of the family to another. We will look at the noble gases, the alkali metals, and the halogens.

The Noble Gas Family

Except for helium, the noble gases each have completely full *s* and *p* orbitals in their outermost energy levels. This gives them 8 electrons in their outermost energy levels, as Table 6-1 shows. Helium, of course, has only one energy level in its ground state, and this energy level is completely filled by the 2 electrons in the 1*s* orbital. Since the noble gases are non-reactive and do not tend to

combine with other elements, we may conclude that their electron arrangements are very stable. This deduction will be important to us as we study the formation of compounds. We shall find that all atoms have a tendency to acquire full outermost energy levels and thus achieve the stable arrangement characteristic of the noble gases.

Electron Configurations of the Noble Gases: a Summary

Name	Atomic Number	Number of Electrons in Energy Levels for Each Principal Quantum Number					
		1	2	3	4	5	6
helium	2	2					
neon	10	2	8				
argon	18	2	8	8			
krypton	36	2	8	18	8		
xenon	54	2	8	18	18	8	
radon	86	2	8	18	32	18	8

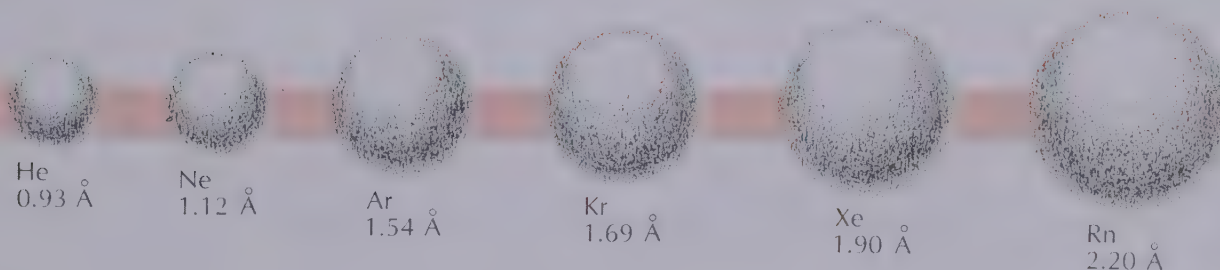
Table 6-1

As the atomic number increases and more electrons are added to the energy levels, it seems that the atomic radius should also increase. Helium has only one energy level, whereas radon has six energy levels and a correspondingly larger atomic radius. Density and atomic weight are proportional, and so we would correctly expect density to increase as atomic weight increases.

Properties of the Noble Gases

Name	Atomic Number	Atomic Radius, Å	Ionization Energy, electron-volts	Melting Point, °C	Density, g/liter at 0°C and 1 atm
helium	2	0.93	24.5	-272	0.18
neon	10	1.12	21.5	-248	0.90
argon	18	1.54	15.8	-189	1.78
krypton	36	1.69	14.0	-156	3.71
xenon	54	1.90	12.1	-111	5.85
radon	86	2.20	10.7	-71	9.73

Table 6-2



Ionization energy, or the energy required to remove the least tightly held electron, decreases as this outer level electron is located farther from the nucleus. The greater the distance from the nucleus, the less the energy needed to pull it away from the atom.

We note that the melting points of the noble gases increase as atomic number increases. We can interpret this to mean that as atoms become heavier and larger, the forces of attraction between them tend to increase, and more energy is required to separate them. What trend would you expect to find in the boiling points of the noble gases?

The Alkali Metal Family

Another family you discovered is one in which the elements have only one electron in the outermost energy level: lithium, sodium, potassium, and rubidium. These elements were also the ones with the *greatest atomic radius* and *lowest ionization energy*. Why? We are not including hydrogen here, because it is not like any other element. Hydrogen almost constitutes a family by itself and will be studied later. However, we should include cesium and francium. This family is called the *alkali metal* family.

You will note that each member of the alkali metal family has the same electron configuration as the preceding member of the noble gas family *plus* one electron which is located in the next higher energy level. Chemical reactions with these elements result in the *loss* of that outermost electron. This loss leaves the ion with a 1+ charge and a stable outermost energy level.

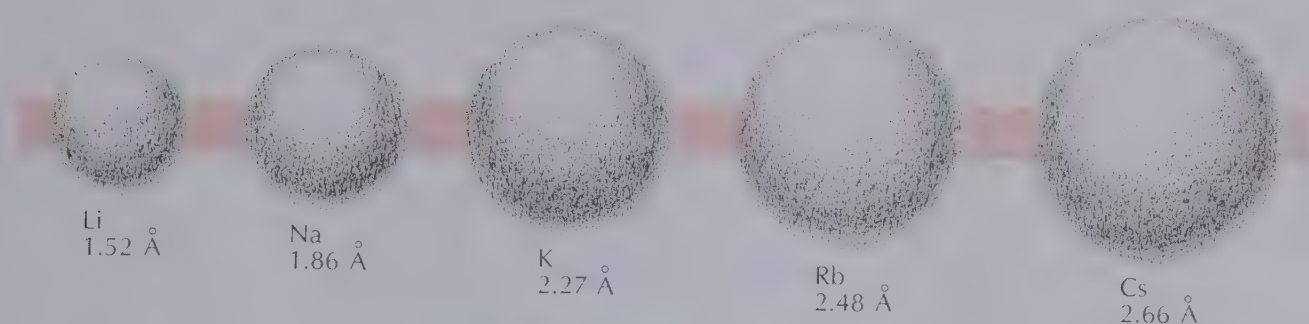
Electron Configurations of the Alkali Metals								
Name	Atomic Number	Number of Electrons in Energy Levels for Each Principal Quantum Number						
		1	2	3	4	5	6	7
lithium	3	2	1					
sodium	11	2	8	1				
potassium	19	2	8	8	1			
rubidium	37	2	8	18	8	1		
cesium	55	2	8	18	18	8	1	
francium	87	2	8	18	32	18	8	1

Table 6-3

As the atomic numbers of the alkali metals increase, we note these trends in properties of the elements (Table 6-4): (1) the atomic radius of the atoms increases as more energy levels are added; (2) the ionization energy decreases as the outer electron becomes farther and farther from the positive nucleus; (3) the melting point decreases. The trend in melting points for the alkali metals is just the opposite from that in the noble gas family.

Properties of the Alkali Metals					
Name	Atomic Number	Atomic Radius, Å	Ionization Energy, electron-volts	Melting Point, C°	Density g/cc
lithium	3	1.52	5.4	179.0	0.53
sodium	11	1.86	5.1	97.7	0.97
potassium	19	2.27	4.4	63.6	0.86
rubidium	37	2.48	4.2	38.8	1.53
cesium	55	2.66	3.9	28.5	1.87

Table 6-4



The Halogen Family

The family of elements preceding the noble gases is commonly called the *halogens*, from a word meaning "salt-former." These are non-metallic elements. The molecules of the halogens contain two atoms; such molecules are said to be *diatomic*. Thus, the formula for chlorine is Cl_2 .

Let us summarize the characteristics of this family and see if we can interpret them on the basis of electron configurations.

Electron Configurations of the Halogens						
Name	Atomic Number	Number of Electrons in Energy Levels for Each Principal Quantum Number				
		1	2	3	4	5
fluorine	9	2	7			
chlorine	17	2	8	7		
bromine	35	2	8	18	7	
iodine	53	2	8	18	18	7

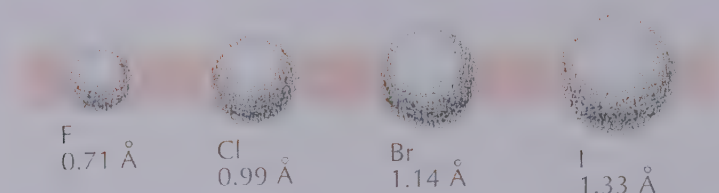
Table 6-5

Each member of the halogen family contains one less electron than the following noble gas. This indicates that in chemical reactions these elements will *gain* an electron, thus giving them the stable outermost energy level characteristic of the noble gases. A gain of one electron will result in the formation of a negatively charged ion.

As the atomic numbers of the halogen family increase, we note these trends in properties of the elements (Table 6-6): (1) the atomic radius of the atoms increases as more energy levels are added; (2) the ionization energy decreases; (3) the melting point increases as atoms become larger and exhibit a stronger attraction for each other.

Properties of the Halogens					
Name	Atomic Number	Atomic Radius, Å	Ionization Energy, electron-volts	Melting Point, C°	Density, g/cc
fluorine	9	0.71	17.3	-219.6	1.54×10^{-3}
chlorine	17	0.99	13.0	-100.9	2.88×10^{-3}
bromine	35	1.14	11.8	-7.2	3.12
iodine	53	1.33	10.4	113.5	4.93

Table 6-6



6-7. THE PERIODIC LAW

From a study of three characteristic families of elements, you can begin to see the value of grouping. Elements with similar electron patterns have similar properties and can be expected to react in a similar fashion in the formation of chemical compounds. Knowing the properties of a few key elements can greatly simplify our study of chemistry. Think what a task it would be to learn the properties of all the known elements. But by grouping the elements into families and by understanding the trends within these families, we can predict with considerable confidence the properties of their compounds.

In the early eighteenth century, as chemists began to identify elements and to study their properties, attempts were made to classify them. The first systems of classification were crude and were based upon atomic weights. By far the most outstanding attempt at classification was made by the Russian chemist, Dmitri Mendeleev. In 1869, he published his Periodic Table of the Elements. Since only about two-thirds of the natural elements had been discovered at that time, the table is a tribute to his insight and scientific ability.

Mendeleev believed that the properties of the elements were a function of their atomic weights. He constructed a table of the known elements with seven elements in each of the first two rows and seventeen elements in each of the next two rows. In order to place elements with similar properties in the same vertical column, several blank spots had to be left. Mendeleev assumed that these gaps indicated elements which had not been discovered. He predicted the properties of such undiscovered elements with surprising accuracy

on the basis of properties of known elements occurring in the same chemical families. His table revealed the fact that if elements were arranged according to increasing atomic weight, their properties were repeated at regular intervals. In other words, properties of the elements are a repeating, or periodic, function of their atomic weights. This statement was called the *periodic law*.

When Moseley discovered that each element has a characteristic number of protons in its atomic nucleus, it was concluded that structure is a better basis for classification than weight. The elements are now arranged according to increasing atomic number, and the same pattern of regularly recurring properties is observed. We now state the periodic law in this way: the physical and chemical properties of the elements are periodic (repeating) functions of their atomic numbers.

6-8. THE MODERN PERIODIC TABLE

The modern periodic table is an attempt to group elements according to properties in order to simplify the study of chemistry. It consists of arranging the elements in order of increasing atomic number so that those with similar outer energy level electron patterns are in the same vertical column. (See next two pages.) The first two columns are made up of elements whose outer *s* orbital is filling. The last six columns are those in which outer *p* orbitals are filling. The middle ten columns are those in which inner *d* orbitals are filling; these elements are known as *transition elements*. Elements in which inner *f* orbitals are filling are placed in horizontal rows at the bottom of most charts to make the arrangement less awkward. The vertical columns of similar elements are called *chemical families*.

The horizontal rows are called *periods* or *series*. These include elements having closely similar orbitals filling with electrons. In general, the periods correspond to the energy levels of an atom. When the last electron enters the outer *p* orbital, we find one of the noble gas elements. There is a large energy gap between this element and the next one because the next electron enters an *s* orbital in the next higher energy level. This difference in energy is denoted by the next element being placed at the beginning of a new period on the table. A new period begins after each of the noble gases.

Periods 2 and 3 each contain eight elements; periods 4 and 5 each contain 18 elements; period 6 contains 32 elements; and period 7 is incomplete at present. In element 20, calcium, the 4*s* orbital has filled and the next ten elements are those in which electrons are being placed in the 3*d* orbitals. The 3*d* orbitals are lower in energy than the 4*p*; hence, they fill first. Element 38, strontium, has its 5*s* orbitals full, so in the next ten elements electrons are entering the 4*d* orbitals. Barium, element 56, has the 6*s* orbital filled, and the next 15 elements are those in which the 4*f* orbitals are filling; 4*f* orbitals are lower in energy than 5*d* orbitals.

The fourteen elements, numbers 58–71, are known as the *lanthanide* series of elements. Elements 90–103 make up a similar series in which 5*f* orbitals are filling; these are known as the *actinide* series.

Periodic Table of the Elements

1 H Hydrogen 1.008

IA	IIA
3 Li Lithium 6.939	4 Be Beryllium 9.012
11 Na Sodium 22.99	12 Mg Magnesium 24.31
19 K Potassium 39.10	20 Ca Calcium 40.08
37 Rb Rubidium 85.47	38 Sr Strontium 87.62
55 Cs Cesium 132.9	56 Ba Barium 137.3
87 Fr Francium (223)	88 Ra Radium (226)

	Alkali metals
	Alkaline earth metals
	Transition elements
	Nonmetals
	Noble gases

22	Atomic number
Ti	Symbol of element
Titanium	Name of element
47.90	Atomic weight (based on ^{12}C scale)

IIIB	IVB	VB	VIB	VIIIB	VIIIB	VIIIB
21 Sc Scandium 44.96	22 Ti Titanium 47.90	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93
39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (99)	44 Ru Ruthenium 101.1	45 Rh Rhodium 102.9
	72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Wolfram 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2

Lanthanide series

57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4
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Actinide series

89 Ac Actinium (227)	90 Th Thorium 232.0	91 Pa Protactinium (231)	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (242)
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										VIIIA
										2 He Helium 4.003
										IIIA IVA VA VIA VIIA
										5 6 7 8 9 10
										B C N O F Ne Boron Carbon Nitrogen Oxygen Fluorine Neon 10.81 12.01 14.00 15.9994 18.998 20.183
										13 14 15 16 17 18
										Al Si P S Cl Ar Aluminum Silicon Phosphorus Sulfur Chlorine Argon 26.98 28.09 30.97 32.06 35.45 39.95
										IB IIB
28 Ni Nickel 58.71	29 Cu Copper 63.54	30 Zn Zinc 65.37	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.91	36 Kr Krypton 83.80		
46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3		
78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (210)	85 At Astatine (210)	86 Rn Radon (222)		

63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
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95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (249)	98 Cf Californium (251)	99 Es Einsteinium (254)	100 Fm Fermium (252)	101 Md Mendelevium (256)	102 No Nobelium (254)	103 Lw Lawrencium (256)
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A comparison of the sizes of the elements in the second row of the periodic table.

Let us summarize some of the characteristics of the periodic table:

1. Elements in a vertical column have similar properties; electron configurations are used to explain this similarity. Such elements make up a chemical family.
2. As the atomic number within a family increases, the atomic radius also increases.
3. As the atomic number within a family increases, the ionization energy decreases.
4. Elements in a horizontal row show a decrease in metallic properties as we read from left to right. Such elements make up a period.
5. As the atomic number increases within a period, the atomic radius tends to decrease because of the increasingly effective nuclear attraction for electrons entering orbitals of about the same energy.
6. As the atomic number increases within a period, the ionization energy increases, although there are irregularities attributed to the pairing of electrons in the outer orbitals.

The convenience of grouping the elements in the periodic table will become more apparent as we begin our study of bonding. This system of grouping is not perfect, and there are exceptions to the generalizations we have stated above. For instance, hydrogen is unique, resembling no other element, and so must be placed somewhat apart from the others. The advantages of the periodic table far outweigh its imperfections, and you may find it to be the most useful single tool in your study of chemistry.

Suggestions for Creative Work

1. Design an original form of the periodic table which provides a convenient grouping for elements with similar properties.

Suggestions for Creative Writing

1. The English chemist, John Newlands, searched for a system of grouping the elements. He said, "The eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music." Comment on this statement and express your views about why this system was doomed to failure.
2. Write a short essay on the role of controversy in the development of science.

Practice Exercises *(Answers on p. 314)*

Note: The subscript to the left of each symbol is the atomic number.

1. Write electron configurations for the following elements:

a. $_{27}\text{Co}$ b. $_{51}\text{Sb}$ c. $_{86}\text{Rn}$ d. $_{80}\text{Hg}$

Chapters 4 and 5 discuss the spectra and spectral lines, the Bohr atom, sub-shells, and the transition elements. Chapter 8 has a good discussion of the photoelectric effect and the photon. The entire series of three volumes is highly recommended for all students.

Ferreira, Ricardo, "Chemists' Involvement in Society," *Chemistry*, February 1971, 18–20.

A human interest sketch of how a great chemist became involved in a bitter political struggle and how it affected his career.

Keller, O. Lewin, Jr., "Predicted Properties of Elements 113 and 114," *Chemistry*, November 1970, 8–11.

An interesting article describing the predicted properties of elements which have not been discovered. It points up the predictive power of the periodic table of elements.

Kogan, Philip, *The Unseen Spectrum*, Ginn and Company, Boston, 1966.

The spectra of elements, quantum numbers, and lasers are presented in an exciting manner. Many colorful diagrams and illustrations.

Morris, Daniel Luzon, "Music of New Spheres," *Chemistry*, December 1969, 10–12.

An unusual discussion on how music may have helped Mendeleev to design the first periodic table. Highly recommended for all students.

Mulliken, Robert S., "Electrons—What They Are and What They Do," *Chemistry*, April 1967, 13–15.

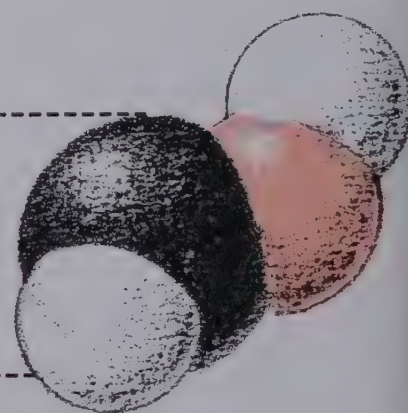
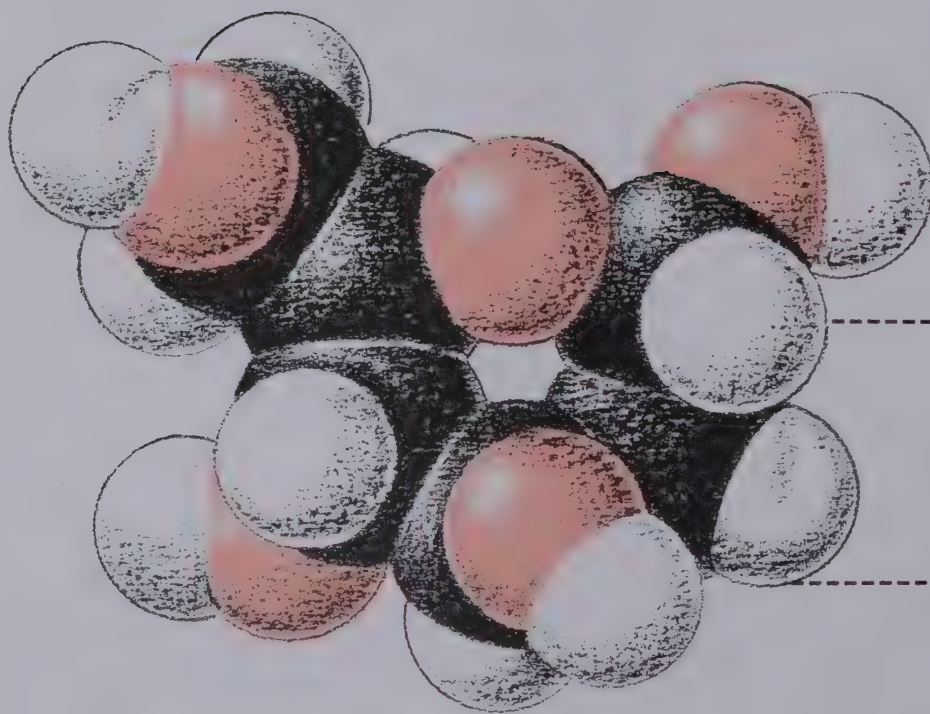
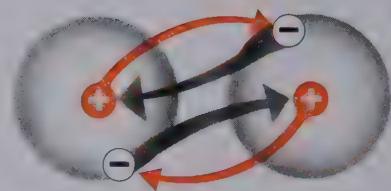
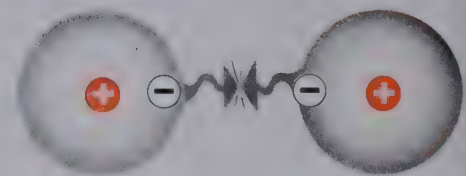
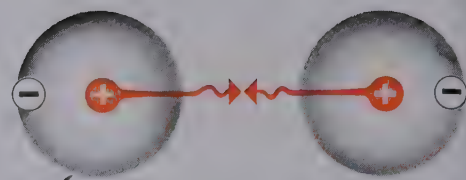
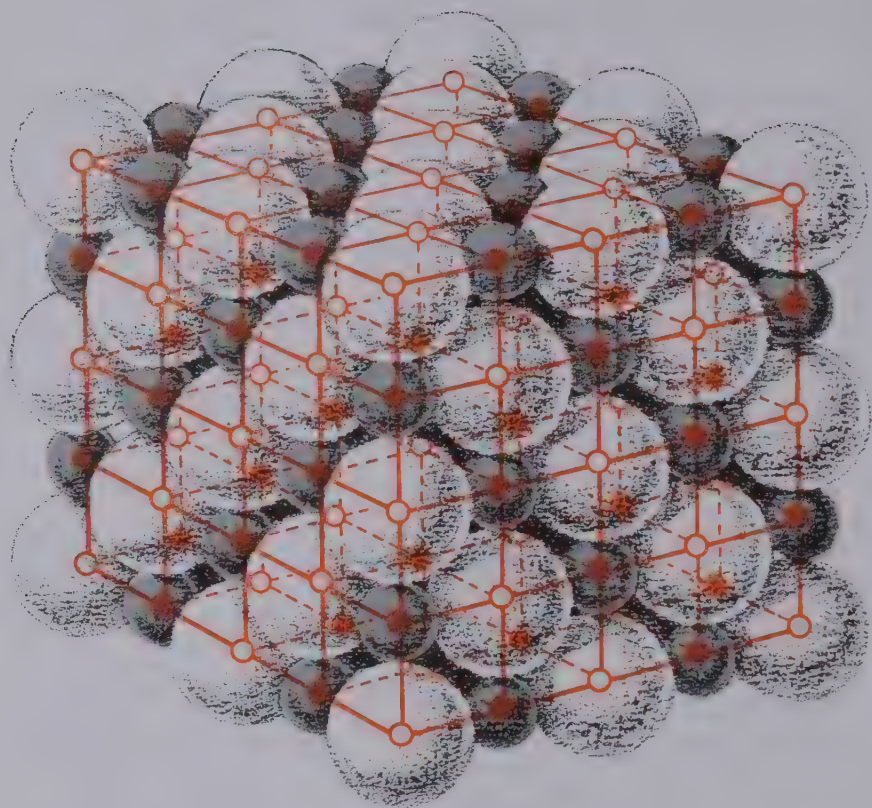
Excellent non-technical discussion. Recommended for all students.

Parsons, Cyril, and Clare Dover, *Elements and Their Order*, Ginn and Company, Boston, 1966.

Presents the periodic properties of elements, the periodic table, chemical families in a graphic and interesting way. Numerous colored illustrations and diagrams. Highly recommended for all students.

Zimmerman, Joan, "Mendeleev—His Own Man," *Chemistry*, December 1969, p. 32.

Another personal glimpse of Mendeleev.





CHEMICAL BONDING

OBJECTIVES:

By the time you have completed your study of Chapter 7, you will be expected to demonstrate acceptable performance on the following objectives.

1. State the accepted definitions for the following terms:
 - a. chemical bond
 - b. ionization energy
 - c. electronegativity
 - d. ionic bond
 - e. polar covalent bond
 - f. nonpolar covalent bond
 - g. oxidation number
 - h. empirical formula
 - i. metallic bond
 - j. hydrogen bond
 - k. dipole
 - l. van der Waals forces
 - m. ion
2. State the requirements for a stable chemical bond.
3. State the effect of increasing atomic number on the atomic radius in (a) chemical families, (b) periods of elements.
4. State the effect of increasing atomic number on ionization energy in (a) chemical families, (b) periods of elements.
5. State a general guideline for determining whether the bond between any two atoms is expected to be nonpolar, polar covalent, or ionic.
6. State the electronegativity trends as the atomic number increases within a period for (a) metals, (b) nonmetals, (c) transition elements.
7. Explain the relationship between bond strength and the melting and boiling points of (a) elements, (b) compounds.
8. State the general properties of compounds formed by ionic bonding.
9. Write the electron dot notation for any compound, given the formula and the name.
10. Explain how hydrogen bonds affect the melting point and the boiling point of compounds.
11. Explain how van der Waals forces affect the melting point and the boiling point of compounds.
12. Predict the formula for a compound formed by any two elements, given the names of the elements, and state the bond type expected.
13. Describe the bonding of two hydrogen atoms to form one molecule of hydrogen gas, H_2 , in terms of energy.
14. Predict the bond type, the formula, and whether the melting point for a compound will be high or low, given a periodic table, a table of electronegativities, and the names of the two elements in the compound.

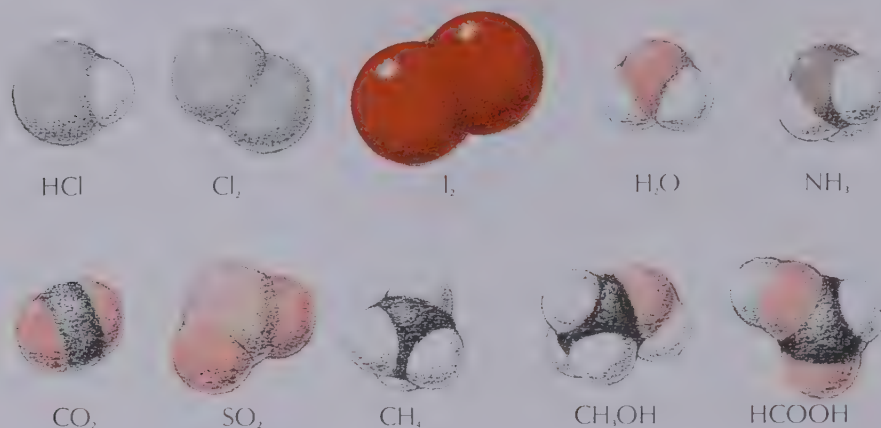
SUGGESTED ORDER OF STUDY

1. Review Exp. 2-5; you will use concepts from it in your study of bond formation.
2. Study Secs. 7-1 thru 7-3.
3. Perform Exp. 7-1. ✓
4. Perform Exp. 7-2. ✓
5. Study Secs. 7-4 and 7-5.
6. Perform Exp. 7-3. ✓
7. Do outside reading.
8. Do the Practice Exercises and review.

9. Take the Self-Test and review as needed.
10. Take test on Chapter 7.

7-1 • PRINCIPLES OF BOND FORMATION

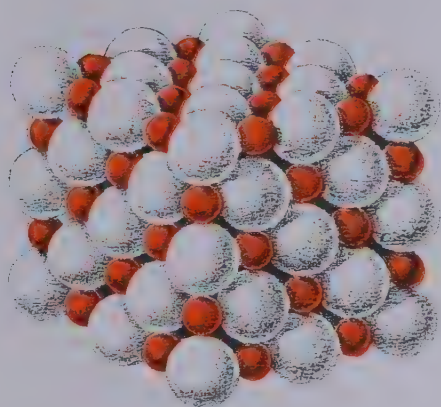
Most atoms do not exist alone; instead, they occur in clusters. These clusters may be atoms of the same element, or they may be atoms of different elements. Properties of elements are really properties of clusters of atoms of that element and not of the individual atoms. It is incorrect to say that oxygen atoms have a density of 1.43 g/liter, and to report that an aluminum atom has a silvery color. Such properties exist only when we consider groups of atoms of these elements. We know that many elements exist in monatomic form, while others are diatomic and still other are polyatomic. The noble gases, for example, are monatomic, and we write their formulas as He, Ne, Ar, Kr, Xe, and Rn. Gases such as oxygen, nitrogen, and hydrogen are diatomic. This is indicated by their formulas, which we write as O_2 , N_2 , and H_2 . The subscript indicates the number of atoms in each molecule of the element. The halogen family is also diatomic and, therefore, their formulas are F_2 , Cl_2 , Br_2 , and I_2 .



Compounds are composed of atoms of different elements. For example, the formula for water is H_2O . This tells us that a molecule of water is composed of two hydrogen atoms in combination with one oxygen atom. Why do hydrogen and oxygen combine in this ratio and not in others? Is it possible to predict the formula for a compound? What determines the ability of certain atoms to combine? How can we explain the known composition of compounds? These are some of the questions we will consider in this chapter.

Any force which tends to hold atoms together is called a *bond*. There are two fundamental principles that will guide us in predicting whether or not a bond will form, and if so, what type it will be. The first of these has to do with energy. *A stable bond will form between atoms only if the resulting combination has less energy than the separate atoms.* The second principle is the *tendency of an atom to acquire the electron configuration of the noble gas nearest to it in the periodic table.* There are other principles which apply and which are used by scientists; however, the two given here are sufficient as you begin to learn about chemical bonding.

At the present time, we have discovered more than 100 elements; the atoms of each of these elements have different electronic configurations. This makes an enormous variety of bonds possible. However, there are only two basic types of energy changes which lead to bond formation. Therefore, chemists have constructed two models which represent these energy changes, and all real bonds are described in terms of these models. The first model is the ionic bond, sometimes called the electrovalent bond, in which *electrons are completely transferred* from one atom to another. The other is the covalent bond, in which *atoms share two or more electrons*. These two models represent extremes; most real bonds can be expected to have characteristics of both. For convenience, however, we will describe bonds in terms of one or the other, depending upon which characteristic predominates.



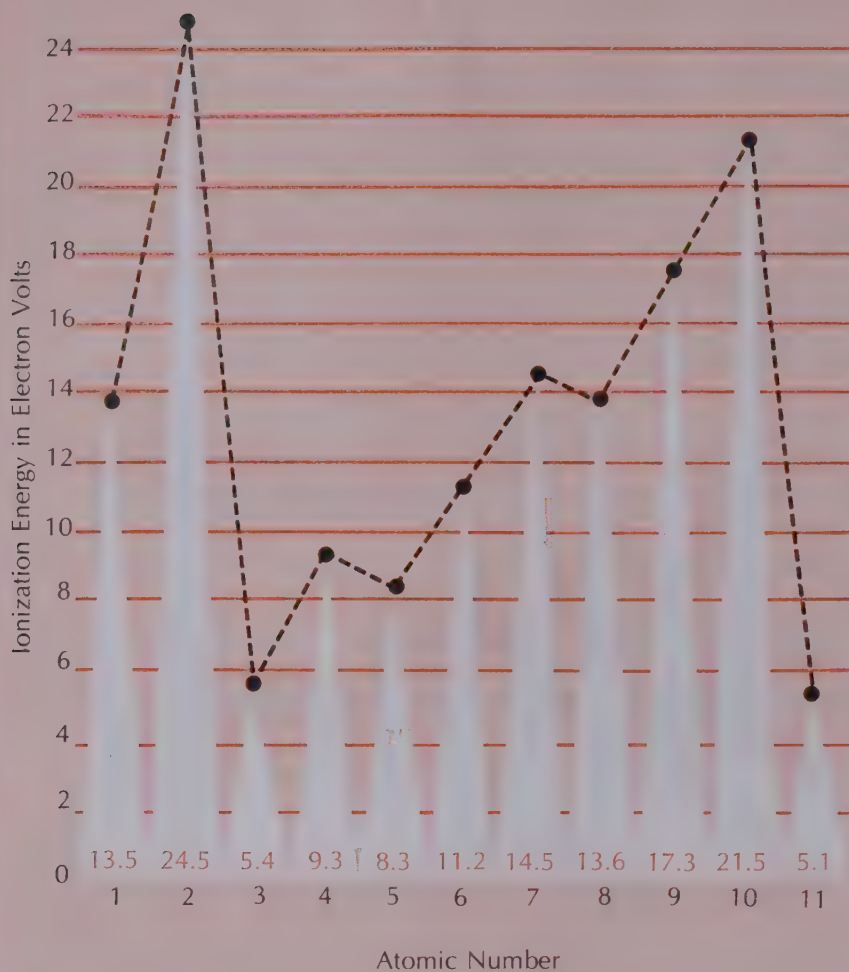
Model of a sodium chloride crystal; an example of ionic bonding.

Since we know that the electron configuration of an element determines its properties, and that similar electron patterns recur at more or less regular intervals when elements are arranged according to increasing atomic number, the periodic table can be very useful in helping us to predict the type of bond that may form between any two elements. We will study three properties of elements that are closely related to atomic number. These are ionization energy, atomic size, and electronegativity. Each of these will be considered before we discuss bond types in detail.

Ionization Energy

In Chapter 6 you learned that ionization energy is the energy required to remove one of the most loosely bound electrons from a neutral atom; this determines the ease with which an atom becomes a positive ion. We have found this to be a periodic property that varies with atomic number. Ionization energy can be measured experimentally by observing the spectrum of light emitted by excited atoms. The value is usually expressed in either of two units. One is the electron-volt and the other is kilocalories per mole of atoms. One electron-volt is the amount of energy corresponding to 3.829×10^{-20} calorie. One electron-volt for one atom is equivalent to 23.06 kcal per mole of atoms. These values are not important for us at this time. The only point to remember is that the electron-volt is a unit in which we measure ionization energy, and the

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$



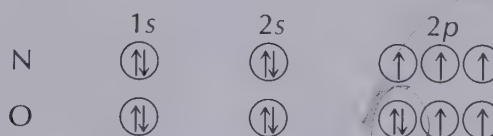
larger the number of electron-volts, the more difficult it is to remove one of the outer electrons from an atom. This will enable you to interpret the values for ionization energy as you study this property of the elements in relation to their atomic numbers.

Ionization energy is influenced by several factors, among which are:

1. *The atomic number of the element.* The greater the nuclear charge, the greater the attraction for outer electrons. Therefore, for elements in the same period of the periodic table, the ionization energy tends to increase as atomic number increases. This occurs because the electrons are being added to the same energy level while nuclear charge is increasing, thus providing a greater attraction for the outer electrons. For example, in period 4, the ionization energy increases from 4.4 electron-volts for potassium to 14.0 electron-volts for krypton. The atomic number of potassium is 19 and that of krypton is 36.
2. *The size of the atom.* This effect is particularly evident in families. As atoms become larger by addition of energy levels, the outermost electrons

are farther from the nucleus. This results in a decreasing attraction and a corresponding decrease in the energy required to remove an electron from the atom. For example, in the alkali metal family, the ionization energy for lithium is 5.4 electron-volts, whereas only 3.9 electron-volts are required to remove the outer *s* electron from the cesium atom, which is much larger than the lithium atom.

3. *Shielding effect of inner energy level electrons.* In larger atoms, the inner energy level electrons tend to shield the outermost electrons from the attraction of the nucleus. This causes the ionization energy to decrease with increasing atomic number. Again, this is especially evident in families. For example, the difference between the ionization energies for lithium and cesium is partially due to this shielding effect of the inner electrons, although some of the effect is caused by the distance of outer energy level electrons from the nucleus. Both factors work together to decrease the ionization energy.
4. *Pairing of electrons in the outer orbitals.* One of a pair of electrons in the same orbital is more easily removed from an atom than one electron which is by itself in an orbital. For example, note the orbital notations for nitrogen and oxygen:



For both elements, the ionization energy is absorbed by the atom when one of the 2*p* electrons is removed. The ionization energy for nitrogen is 14.5 electron-volts, but the ionization energy for oxygen is 13.6 electron-volts. Offhand, you would think that the ionization energy for oxygen would be higher, since it has 8 protons in its nucleus, compared to 7 protons in the nucleus of a nitrogen atom. This shows how much easier it is to remove an electron from an orbital if another electron is still left behind in the same orbital, compared to the case where the orbital is emptied by removing one electron.

Problem:

Draw the orbital notations for phosphorus and sulfur; predict which element has the higher ionization energy.

Atomic Size

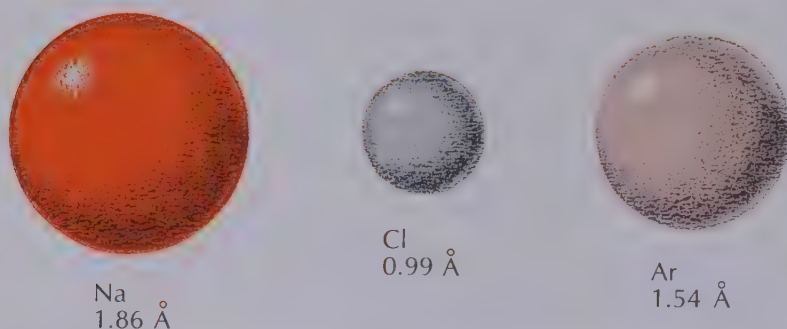
There is some disagreement among authorities about atomic size. This is partly because the sizes are difficult to measure and partly because the sizes of ions vary in different compounds. However, you have observed that when atomic radii are plotted against atomic number, there is much evidence of periodicity in the elements. We can summarize the trends in this way:

1. The atoms in a chemical *family* increase in size as the atomic number increases. This is due to the addition of more energy levels as greater numbers of electrons are added to the atom.

2. In any given *period*, the atomic size tends to decrease as atomic number increases. This is because electrons are being added to the same energy level while nuclear charge is increasing. The higher nuclear charge pulls the outer electrons closer to the nucleus, and this results in a smaller atomic size.

The radius of a sodium atom is 1.86 \AA . As we proceed across the period beginning with sodium in the periodic table, the size of the atoms shows a decreasing trend, from left to right. Chlorine, on the right, for example, has an atomic radius of 0.99 \AA . The sizes of all these atoms in this period, from sodium through chlorine, can be measured in similar ways. But because argon, on the extreme right of this period, is not yet known to form compounds with other elements, the size of the argon atoms must be measured in a different way. The measured radius of an argon atom is 1.54 \AA . Maybe, if we could measure the atomic radii of all of the elements from sodium through argon in the same way, argon would turn out to be the smallest of all. Or, perhaps it would turn out to be larger than chlorine, as the measurements that can be made now seem to indicate. At this time, these questions cannot be answered.

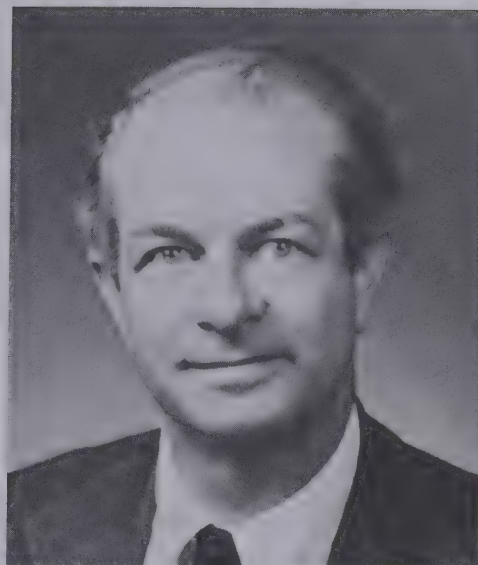
We will find that atomic size is an important factor in determining bond type.



How can you account for the size variation among these three atoms?

Electronegativity

Another property of atoms which is even more useful in determining bond types is called *electronegativity*. Chemists had long known that certain atoms were more likely than others to attract electrons in forming a chemical bond. Linus Pauling (1901–) assigned values to the elements which indicate the tendency of their atoms to attract electrons. Atoms with a high electronegativity value have a strong attraction for electrons; those with low electronegativity values exhibit a weak attraction for electrons. By using the electronegativity difference between two atoms, we can predict the type of bond that these atoms will form in a chemical reaction, as we will see in Secs. 7-2 and 7-3.



The development of the electronegativity concept is only one among many of Linus Pauling's contributions to chemistry and to human understanding in general. He is a two-time winner of the Nobel Prize, once in 1954 for his work in chemistry and then again in 1962 for his efforts to further the cause of world peace.

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Electronegativity Values Represent an Arbitrary Scale to Indicate the Attraction of an Atom for Electrons Involved in the Formation of a Chemical Bond.

Lanthanide Series	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide Series	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Periodic Table of Electronegativities

Table 7-1

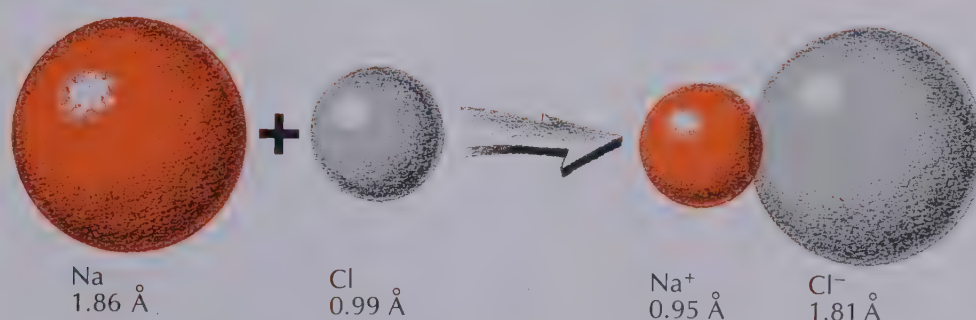
Look at Table 7-1, the periodic table of electronegativities. Notice the trends that become apparent:

1. Electronegativity tends to decrease with increasing atomic number in the chemical families. In Group IA, francium (0.7) has less tendency to attract electrons than lithium (1.0).
2. Metals have low electronegativity values and nonmetals have high electronegativity values. Compare sodium (0.9) in Group IA with chlorine (3.0) in Group VIIA.
3. Electronegativity tends to increase with increasing atomic number within a *period* and reaches a maximum for the halogens. For the 5th period, notice the increase from rubidium (0.8) to iodine (2.5).
4. Transition elements vary only slightly in electronegativity. See the B groups in the center of the table.
5. Noble gases are not usually assigned electronegativity values because they do not tend to form very many different chemical bonds.

The electronegativity values shown in Table 7-1 are not to be memorized. However, we will refer to them throughout our study of bonding, so you should keep the trends in mind.

7-2. THE IONIC BOND

The model of a chemical bond formed by transfer of electrons from one atom to another is called an *ionic bond*. Since atoms are neutral, this loss or gain of electrons results in charged particles which we call ions; hence, the name ionic bond. The greater the electronegativity difference between the two atoms, the more ionic the bond. For this reason, the elements that are in Groups IA and IIA tend to unite with the elements in Groups VIA and VIIA by electron transfer to form ionic bonds. A rule of thumb quite helpful in determining whether an ionic bond will form between two elements is: If the electronegativity difference is 1.8 or greater, you can call the bond ionic and few chemists will argue with you. Since it is a rule of thumb, there are exceptions to this generalization, but it can be helpful in making predictions about bond types.



Note the changes in size as atoms become ions.

Let's apply the principles we have discussed to the formation of sodium chloride from atoms of sodium and chlorine. Sodium has an electronegativity of 0.9, and the electronegativity of chlorine is 3.0. The electronegativity difference is 2.1, so we predict the bond to be ionic. The formation of an ionic bond from atoms can be visualized in three steps (energies are given in kilocalories per mole of atoms):

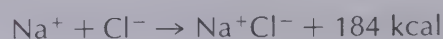
1. The first step is endothermic and requires sufficient ionization energy to remove the 3s electron from a sodium atom to form a sodium ion:



2. The second step is exothermic and releases energy; the electron is accepted by a chlorine atom:



3. The third step is also exothermic and releases energy as ions attract each other while moving into orderly positions in the crystal:



A stable ionic bond forms because the total energy released in steps 2 and 3 is greater than the energy absorbed in step 1. (We use a plus sign for energy that is absorbed and a minus sign for energy that is released.)

Step 2	— 87 kcal
Step 3	<u>—184 kcal</u>
	—271 kcal, energy released
Step 1	<u>+118 kcal</u> , energy absorbed
	—153 kcal, net energy released per mole of NaCl formed from atoms of sodium and chlorine.

The number of electrons lost by one atom must be equal to the number gained by another atom in forming the ionic bond. The sodium atom loses a 3s electron and acquires the electron configuration of neon. At the same time this electron moves into a 3p orbital of the chlorine atom, giving it the electron configuration of argon. We can represent this electron transfer by orbital notation or by electron dot notation, whichever is more convenient.

Orbital Notation

Atom	1s	2s	2p	3s	3p
Na	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	\uparrow	$\circ \circ \circ$
Cl	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow$
Ion					
Na ⁺	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	\circ	$\circ \circ \circ$
Cl ⁻	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$

Electron Dot Notation



In a more complicated example of ionic bonds, calcium forms an ionic bond with chlorine in this manner:

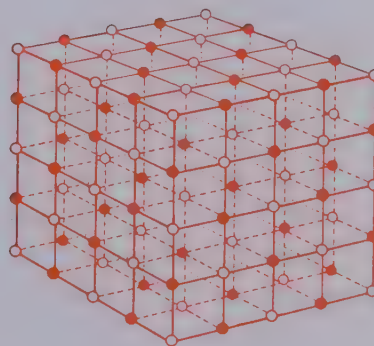
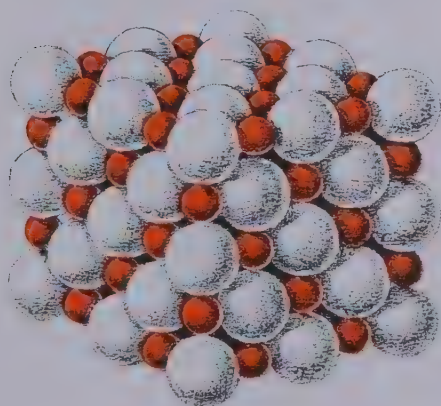
1. $\text{Energy} + \text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^{-}$
2. $2\text{e}^{-} + \text{Cl}_2 \rightarrow 2\text{Cl}^{-} + \text{energy}$
3. $\text{Ca}^{2+} + 2\text{Cl}^{-} \rightarrow \text{Ca}^{2+}(\text{Cl}^{-})_2 + \text{energy}$

The calcium atom has an outer electron configuration of $4s^2$. Therefore, sufficient energy must be supplied to remove both $4s$ electrons. This permits Ca^{2+} to acquire the octet configuration of argon. Each chlorine atom requires only one electron to fill the $3p$ orbitals, and so two chlorine atoms must be used for each calcium atom to balance electrons lost with electrons gained. In the crystal arrangement of CaCl_2 , there is one doubly charged (positive) calcium ion for each two singly charged (negative) chloride ions. The electronegativity difference is 2.0, which indicates that the bond is ionic according to our rule of thumb. The calcium atom forms a smaller ion, while the chlorine atoms form larger ions.

Empirical Formulas

The formula for sodium chloride is NaCl , but we cannot speak of molecules of sodium chloride, for they do not exist. It is true that the ratio of Na^{+} ions to Cl^{-} ions in a crystal of sodium chloride is 1:1, but we do not know which Na^{+} ion belongs to which Cl^{-} ion. Both kinds of ions exist together in clusters within an orderly arrangement which we call a crystal or a macromolecule. Therefore, the formula NaCl is known as an *empirical formula*. Empirical formulas tell us the simplest ratio in which ions exist in an ionic compound.

The ions formed in ionic bonding are held together by the electrostatic force of attraction among oppositely charged particles. This force of attraction is proportional to the amount of charge and inversely proportional to the square of the distance between the centers of the ions. That is, the greater the ionic charge and the smaller the ionic radius, the stronger the bond. The electrostatic force exerted by an ion extends equally in all directions. The number of positive ions which can be attracted to a negative ion depends only upon the space available around the negative ion, and conversely. In the case of sodium chloride, each chloride ion is surrounded by six sodium ions, and each sodium ion is surrounded by six chloride ions. The structure of crystals will be considered in more detail in a later chapter.



Effect of Ionic Radius

In Chapter 2 you performed an experiment which showed that when unlike charges approach each other, the potential energy of the system decreases. This is a useful concept in bonding. In crystals formed by ionic bonding, the distance between ions adjacent to each other is the distance which represents minimum potential energy. Such distances have been determined by special techniques, among which the most important is x-ray diffraction.

The larger the ionic radius, the greater the distance between the centers of adjacent ions and the smaller the attractive force. The importance of ionic radius can be appreciated if we compare sodium chloride with cesium chloride. Both sodium and cesium belong to the Group IA metals, but cesium has the larger atomic radius. The distance between the center of a cesium ion and the center of a chloride ion is much greater than that between a sodium ion and a chloride ion. As a result, the attraction among the cesium ions and the chloride ions is much less, and a weaker ionic bond is formed. This can be verified by comparing the melting points of the two crystals. Melting point is a measure of bond strength in that the weaker bonds require less energy to separate them and, consequently, the melting point of such solids is lower. The melting point of NaCl is 801°C , whereas the melting point of CsCl is 646°C . Weaker bonds indicate less stable compounds. Let us compare the melting point of the Group IA elements in combination with the element chlorine, which is found in Group VIIA.

**Relationship between Ionic Size and Melting Temperature
for Chloride Compounds of Group IA Elements**

Compound	+ Ionic Radius, Å	- Ionic Radius, Å	Melting Temperature, $^{\circ}\text{C}$
NaCl	0.95	1.81	801
KCl	1.33	1.81	776
RbCl	1.48	1.81	715
CsCl	1.69	1.81	646

Table 7-2

In summary, we can say that ionic compounds:

1. Are formed by elements in Groups IA and IIA uniting with elements in Groups VIA and VIIA.
2. Are composed of ions having the noble gas electron configurations.
3. Are held together by forces of electrostatic attraction.
4. Have high melting and boiling points.

Problems:

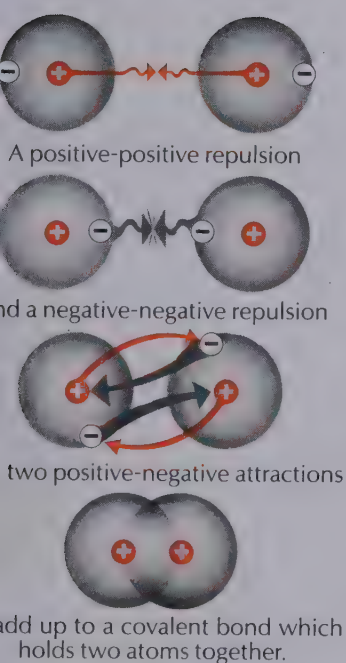
1. Write the three-step reaction for the formation of magnesium oxide.
2. Represent the reaction by orbital notation.
3. Represent the reaction by electron dot notation.

4. Complete the following table by qualitatively predicting the missing melting temperatures.

Relationship between Ionic Size and Melting Temperature for Sodium Compounds of the Group VIIA Elements			
Compound	+ Ionic Radius, Å	– Ionic Radius, Å	Melting Temperature, °C
NaF	0.95	1.36	801
NaCl	0.95	1.81	
NaBr	0.95	1.95	
NaI	0.95	2.16	

7-3 · THE COVALENT BOND

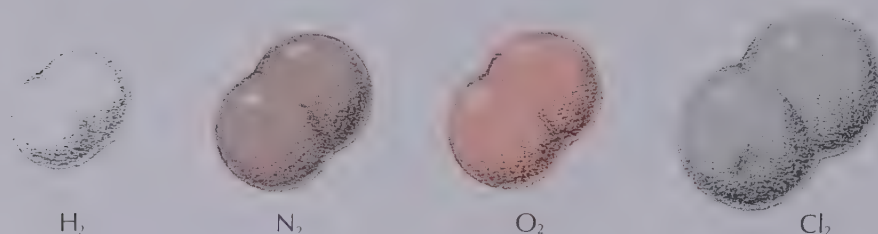
In our model of covalent bonding, electrons are not transferred from one atom to another, but are shared by the bonded atoms. The word *covalent* comes from Latin roots, *co-* and *valens*, which literally mean “strong through sharing.” If atoms are to share electrons, they must approach each other closely enough for their electron orbitals to overlap. Consider the bonding of two hydrogen atoms as a basic example. Each hydrogen has one 1s electron. In order to achieve the electron configuration of helium, the noble gas nearest to hydrogen in the periodic table, a hydrogen atom must have two electrons in the 1s orbital. As two hydrogen atoms approach each other, the forces of attraction are greater than the forces of repulsion, and the atoms come close enough for the 1s orbitals to overlap and for the two atoms to share the two electrons. This gives both atoms the electron configuration of helium, which is a stable arrangement. The potential energy of the two atoms is lower when they are closer together than when they are far apart; the atoms give up energy and form a covalent bond. Here we find an example of low energy being predominant over maximum randomness. Separate atoms represent a more random arrangement than bonded atoms.



Up to very short distances, as two hydrogen atoms approach each other, the forces of attraction increase and the potential energy decreases. As they approach very closely, however, the repulsive forces cause the potential energy to increase. At the distance where attractive forces and repulsive forces are balanced, potential energy is at a minimum. A covalent bond is formed between the two atoms, and we have a molecule of hydrogen, H_2 . This optimum distance is achieved when the two shared electrons are most probably located between the two positive nuclei. At this distance, both electrons are attracted by both nuclei, and the nuclei are shielded from each other by the overlapping electron orbitals. Also notice that the two electrons occupy the same 1s orbitals, so they must have opposite spins. Under these conditions a stable covalent bond forms between the hydrogen atoms.

Nonpolar Covalent Bonds

When two identical atoms give up energy to form a covalent bond, each atom has the same nuclear charge and the same attraction for the shared electrons and, therefore, the same electronegativity. Such bonds are called nonpolar covalent bonds. Hydrogen, nitrogen, oxygen, and the halogen family elements

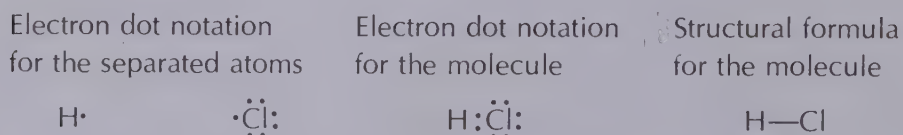


all form molecules with stable, nonpolar covalent bonds. The molecules of these elements represent a more stable arrangement than separate atoms of the same elements because they have less energy.

Polar Covalent Bonds

Most covalent bonds are formed between unlike atoms. When atoms are unlike, they have different electronegativities and do not share the electrons of a bond equally. We need a criterion to determine which atoms in the bond have a greater attraction for the shared electrons. The concept of electronegativity provides this guideline. Let us consider the case of bonding between a hydrogen atom and a chlorine atom to form a molecule of hydrogen chloride.

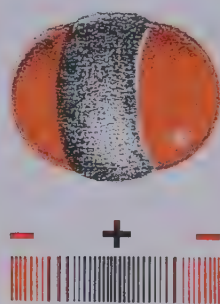
Hydrogen has an electronegativity of 2.1 and chlorine has an electronegativity of 3.0. This indicates that the chlorine atom has a greater attraction for electrons than does the hydrogen atom. When these two atoms approach closely enough to allow the 1s electron orbital of hydrogen to overlap the half-filled 3p orbital of chlorine, the two shared electrons will be attracted more strongly toward the chlorine nucleus than toward the hydrogen nucleus. The result is that the chlorine end of the molecule acquires a partial negative value, while the hydrogen end of the molecule acquires a partial positive value.



The result is a covalent bond that exhibits some ionic character. Such bonds are called *polar* covalent bonds, meaning there are two regions in the molecule which have certain characteristics of electrical poles. Again, we need to remind ourselves that the concepts of ionic and covalent bonds are models which represent the two extremes in energy changes that occur when atoms bond. Most real bonds have characteristics of both, and we classify a particular bond on the basis of the model it most closely resembles.

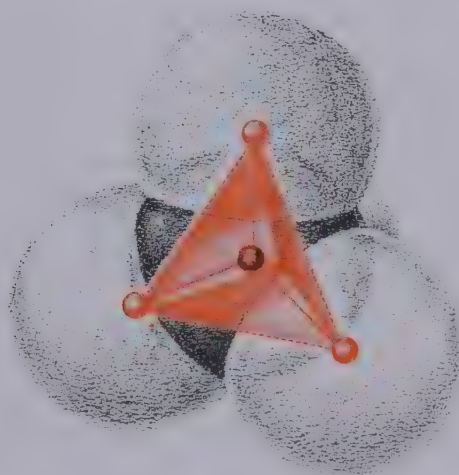
By way of generalization, we can say that (with some exceptions) all chemical bonds between elements other than those in Groups IA and IIA with Groups VIA and VIIA are expected to be covalent. All covalent bonds are polar except when like atoms bond.

There are no examples of nonpolar covalent bonding between unlike atoms. This is because of the difference in electronegativity between any two unlike atoms. If the difference in electronegativity is not too large, a polar covalent bond can be expected. The molecule that is formed will have a partly positive end and a partly negative end. The polar covalent bond often produces a polar molecule. However, sometimes we can have polar covalent bonds and a nonpolar molecule. Consider carbon dioxide, for example. This molecule is composed of a carbon atom in the middle, and one oxygen atom on each end:

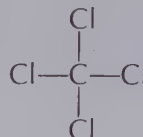


The two polar bonds are opposed to each other. If we imagine that the polar covalent bond is an arrow pointing from the plus to the minus, then for carbon dioxide the arrows point in opposite directions and can be imagined to cancel each other. In such cases the bonds are polar covalent, but the molecule is nonpolar.

Another example is the molecule carbon tetrachloride, which has four polar covalent bonds but is itself nonpolar. In this molecule one carbon atom is in the middle and four chlorine atoms are at the corners of a tetrahedron. The electronegativity difference between carbon and chlorine is 0.5. Therefore, each $\text{C}-\text{Cl}$ bond is polar, with the chlorine partly negative and the carbon partly positive. The fact that four identical polar bonds are distributed in a symmetrical arrangement results in a nonpolar molecule.



Bonding in which electrons are shared is commonly represented by electron dot notation or by drawing a line between the bonded atoms. A single line between atoms indicates that one pair of electrons is shared; two lines mean that two pairs of electrons are shared. Such a representation is called a *structural formula*. You have noticed these structural formulas already, for H_2 and HCl ; here is the electron dot notation and the structural formula for CCl_4 . Actually, these representations should not be flat as they are on the paper, but three dimensional, something like the illustration on the previous page.

Electron Dot Notation, CCl_4 Structural Formula, CCl_4 

Problems:

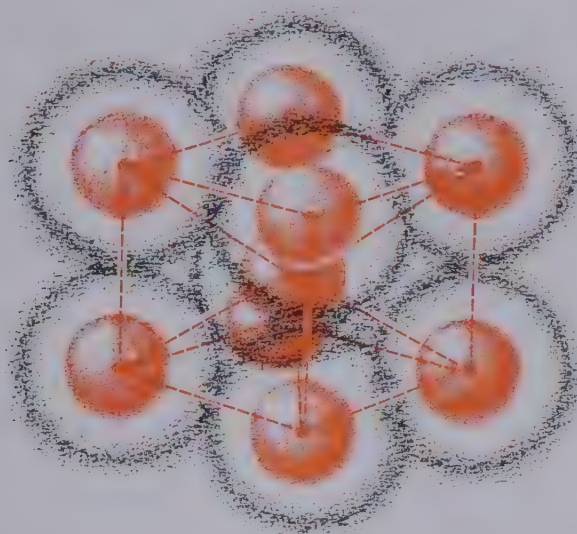
1. Methane, CH_4 , which is natural gas, is formed by polar covalent bonding between carbon and hydrogen. Draw the electron configuration for these atoms.
2. Represent the bonding for methane by electron dot notation.
3. Represent the bonding for methane by a structural formula.

7-4 • METALLIC BONDS

Metals are characterized by luster, the ability to conduct electricity, ductility, and malleability. Ductility is the property which enables a metal to be drawn into a thin wire. Malleability is the property which enables a metal to be rolled into sheets. These properties are not found in covalent and ionic substances. To explain the behavior of the pure metals, a third type of bonding called *metallic bonding* can be described.

If you examine the electron configurations of the metals, you will find that they have a number of unoccupied orbitals in the outermost energy level. This means that relatively few, loosely held, electrons have many other orbitals which they can occupy on other nearby atoms by gaining or losing a very small amount of energy. That is, in the solid metal the orbitals of adjacent atoms overlap so that electrons can readily move from atom to atom and, therefore, throughout a single piece of metal. We can view these loosely held electrons as not occupying a specific region near each of the atoms in the metal. Instead, they are free to move about within the whole piece of metal.

In most metals each atom is surrounded by as many as twelve other atoms. So, inside the piece of metal, we can imagine that there are atoms which have more or less lost some of their electrons, perhaps one or two. Or, each of the atoms is sharing one or two of its electrons with the other atoms. One way or another, the mental picture is that of many loose electrons batting about inside the metal, in and around what is left of the atoms. The electrostatic attrac-



A model of the crystal lattice for sodium metal. Note the orbital overlap.

tions among the positive nuclei of the atoms and the freely roving electrons constitute the metallic bonds.

Metallic bonds are usually quite strong, as indicated by the relatively high melting and boiling points of the transition metals, by the hardness of many metals, and by the strength of some metals when you try to pull the atoms apart. You know that it is easier to pull a piece of string apart, for example, than to pull even a very fine wire into two pieces.

Because many electrons are free to move about in the crystal, pressure or stress does not cause shattering as it does in ionic crystals. As atoms in a plane are moved out of position, another group of atoms slides in to replace them, thereby maintaining the strength of the metal. This accounts for the ductility and malleability of many metals.

The ability of the mobile electrons to move readily through the metal also explains the electrical and heat conducting properties of metals.

7-5 • BONDS BETWEEN MOLECULES

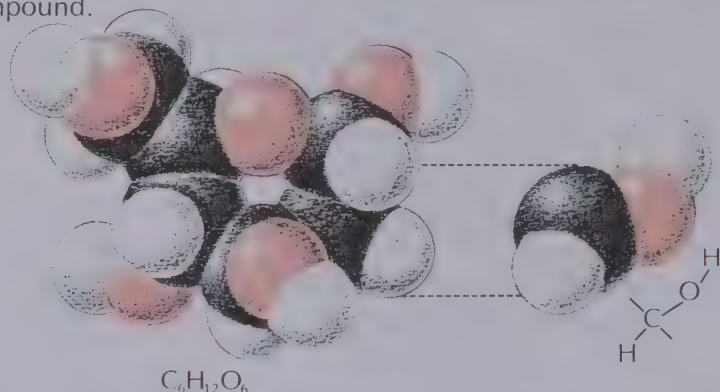
The ionic, covalent, and metallic bonds are our ways of referring to the forces that hold atoms together as molecules or as groups of ions. There are also forces which act between molecules to hold them together. We know that such forces must exist, because even the gases with one atom per molecule can be liquefied and eventually solidified. We also know that most molecular substances can be melted and vaporized without losing their identity. The melting or vaporizing of substances causes separate, whole molecules to leave the other molecules. We will consider briefly two types of intermolecular forces which, although much weaker than those found in bonding between atoms, are quite important in understanding the properties of molecular substances.

Van der Waals Forces

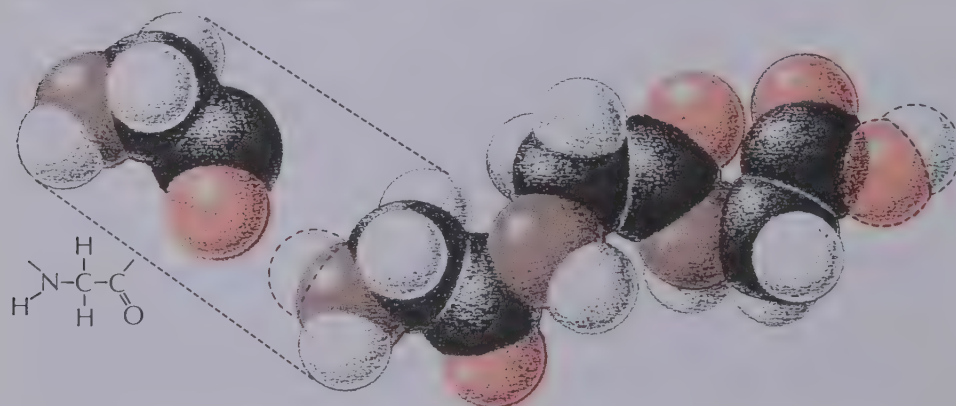
Ionic compounds are composed of ions, some positively and some negatively charged. Any one ion has a few, or more, oppositely charged ions near it, and each of these has other oppositely charged ions nearby, and so on. The electrostatic forces between and among all the ions in a crystal hold all of them together in one piece. Salt is a good example of an ionic substance.

But, what about molecules? What holds one molecule to another molecule? You know that sugar is a solid. In each small crystal of sugar there are millions upon millions of molecules, all held together to form the piece of sugar. What holds them together?

We can get a clue by noticing that salt has a higher melting point than sugar. The forces that hold sugar molecules together, then, are probably weaker than the forces holding the ions in salt together. One model that is used to explain these weak forces involves the polar covalent bonds in the sugar molecules. Some parts of the sugar molecule are partly positive, others partly negative. Each sugar molecule has half a dozen or more of these partly charged parts, as you might guess from the structural formula for glucose (one kind of sugar). The partly positive and partly negative parts of one sugar molecule attract the partly negative and partly positive parts of other, nearby sugar molecules, and these, in turn, do the same to other nearby molecules. In this way, all are held together, but the forces are weak compared to those in an ionic compound.



Glucose (top) and a segment of a chain made from glycine molecules (bottom) are fairly complex structures containing many atoms and many bonds. Glucose is made of units of $HCOH$, the glycine chain of units of NC_2H_3O . Identify points on these molecules where they will be polar.



Weak forces such as these which hold molecules together are called van der Waals forces. Johannes van der Waals, a Dutch physicist, was the first scientist to suggest that these attractive forces might exist. He made his suggestion in 1873; since then these attractive forces have been called van der Waals forces. Actually, van der Waals only suggested that such forces might exist; he did not think of the model that we have described. Other scientists did that.

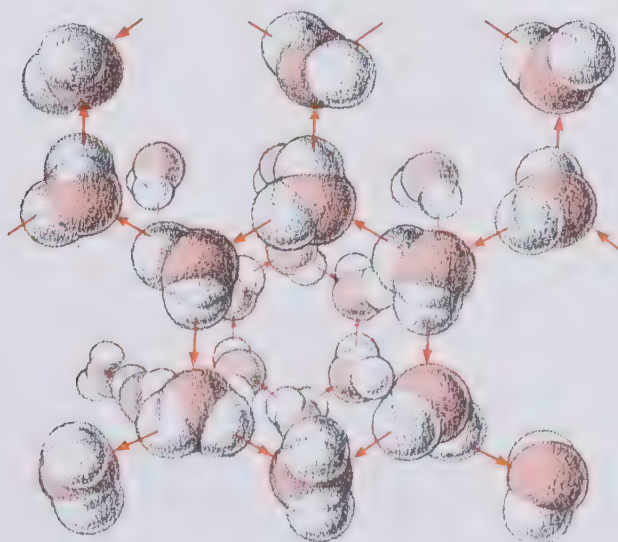
The strength of van der Waals forces is largely determined by the size and shape of the molecule. Other factors being equal, large molecules attract each other with greater force than do small molecules.

Van der Waals forces are present in all substances, but are usually overlooked because of the much stronger forces also present. We mention them here so that you are aware that such forces do exist and that in some cases they are important in explaining observed properties.

Hydrogen Bonds

A few polar covalent compounds have melting and boiling points which are too high to be explained on the basis of van der Waals forces. Some of these compounds contain hydrogen atoms that are bonded to highly electronegative atoms, such as oxygen, nitrogen, or fluorine atoms. When this happens, the hydrogen electron is attracted so strongly to the electronegative atom that the hydrogen atom protrudes from the molecule as a site of distinctly positive polarity which is attracted to the negative end of other polar molecules.

Chlorine has an electronegativity of 3.0 and hydrogen's is 2.1. In HCl the chlorine atom attracts the hydrogen electron so strongly that the hydrogen atom is almost like an exposed proton. This positively charged end of the HCl molecule exerts an attractive force on the negative chlorine end of another HCl molecule nearby. This makes it difficult to separate the molecules. Hence, the melting and boiling points are abnormally high. Water and ammonia are examples of compounds in which hydrogen bonding has a noticeable effect upon observed properties. Table 7-3 summarizes the types of bonds found between atoms and molecules of various substances.



Identify the hydrogen bonds in this representation of water molecules in an ice crystal.

Summary of Bond Types				
	Type	How Formed	Examples	Associated Properties
Bonds between Atoms	1. Ionic	Transfer of electrons from one atom to another: results in electrostatic attraction of ions.	NaCl, MgO	Form crystals; high melting and boiling points; electrical conductors in liquid state.
	2. Covalent (a) polar	Sharing of electrons Unequal sharing, resulting in regions of charge	HCl, H ₂ O	Strong, stable bonds; non-conductors of electricity in any form.
	(b) nonpolar	Equal sharing, as with like atoms; no regions of charge	H ₂ , Cl ₂	
	3. Metallic	Sharing of many, many mobile electrons within a metal	Cu, Zn	Highly lustrous, ductile, malleable, good electrical conductors.
Bonds between Molecules	4. van der Waals	Weak electrical attraction caused by small temporary or permanent charges on other molecules.	He, H ₂ , C ₆ H ₁₂ O ₆	Low melting and boiling points; gaseous state can be converted to liquid or solid.
	5. Hydrogen	Attraction of negative ends of polar molecules by exposed protons on other molecules.	HCl, NH ₃ , H ₂ O	Unusually high melting and boiling points for the molecular size.



Table 7-3

Suggestions for Creative Work

1. We have presented two models to explain the types of chemical bonds. Think of different models which would serve this purpose.
2. The boiling point of ammonia, NH₃, is -33°C , while the boiling point of water, H₂O, is 100°C . Think of an explanation that accounts for the difference in boiling points.

Suggestions for Creative Writing

1. In science, it frequently happens that independent workers in widely separated geographic areas make simultaneous discoveries. Write an essay in which you advance possible reasons for this occurrence.
2. Write an essay on the importance of freedom in the advancement of science.

Practice Exercises (Answers on pp. 316, 317)

1. State the accepted definition for:
 - a. chemical bond
 - b. electronegativity
 - c. ionization energy
 - d. hydrogen bond
2. Explain the effect of increasing atomic number on ionization energy in:
 - a. the halogen family
 - b. period 3
3. Explain the effect of increasing atomic number on the atomic radius in:
 - a. Group 1A
 - b. period 4
4. Using a table of electronegativities, indicate whether the following bonds will be ionic, polar covalent, or nonpolar covalent:
 - a. O—Cl
 - b. N—N
 - c. Rb—Cl
 - d. C—H
5. State the bond type that can be expected between atoms in the following substances:
 - a. CaCl_2
 - b. CaO
 - c. NO_2
 - d. HF
6. Draw electron dot diagrams for:
 - a. MgCl_2
 - b. Cl_2
 - c. BeO
 - d. H_2O
7. Which of the following compounds probably has the highest melting point? Cite a reason for your answer.
 - a. NaCl
 - b. KCl
 - c. RbCl
8. Explain how hydrogen bonding affects the melting point of a compound.
9. State the electronegativity trends for:
 - a. metals
 - b. nonmetals
 - c. transition elements
10. State the general properties usually associated with compounds formed by ionic bonding.
11. Predict the chemical formulas for the following compounds and state the expected bond type for each:
 - a. copper chloride
 - b. magnesium bromide
 - c. aluminum oxide
 - d. hydrogen sulfide
 - e. carbon dioxide
12. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION	REASON
In general, the electronegativity values tend to decrease with increasing atomic number within a period	Because the atomic radius is becoming smaller and the atom exhibits less attraction for electrons.

Self-Test (Answers on pp. 317, 318)

1. NaCl has a melting point of 801°C ; NaF has a melting point of 988°C . Account for this difference.
2. Classify the following into two groups: those with predominantly ionic bonds, and those with predominantly covalent bonds.
 - a. Rb_2O
 - b. CaCl_2
 - c. NaI
 - d. SO_2
 - e. BaO

3. State the accepted definitions for:
 - a. chemical bond
 - b. van der Waals forces
 - c. ionic bond
 - d. empirical formula
 - e. ion
4. Draw electron dot diagrams for:
 - a. CO_2
 - b. H_2S
 - c. AgCl
 - d. H_2
5. State the requirements for a stable chemical bond.
6. Which bond type is responsible for the lowest melting points of compounds?
7. State the electronegativity trend for the nonmetals.
8. Which has less energy, two separated oxygen atoms or an oxygen molecule (O_2)? Cite reasons for your answer.
9. Predict the chemical formulas for the following substances and state the expected bond type between atoms for each:
 - a. chlorine
 - b. potassium iodide
 - c. calcium chloride
 - d. copper sulfide
 - e. aluminum chloride
10. (Multiple Completion; see special directions in Appendix 13)
Compounds in which the bonds are mainly covalent are
 1. CsCl
 2. CH_4
 3. LiF
 4. SO_2

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Based on a paper presented at the International Conference on Chemistry Teaching in Buenos Aires in June, 1965. Relates theory to observation. Discusses bond types and bond angles, structure of elements in relation to their compounds. Easy reading and very informative.

Bent, Henry A., "The Tetrahedral Atom," *Chemistry*, January 1967, 8-15.

Discusses the effect of the Pauli Exclusion Principle, electron clouds, rotational energies of molecules. Uses cut-and-paste models. Has diagrams and a bibliography. Recommended for the serious student.

Ferreira, Ricardo, "Molecular Orbital Theory," *Chemistry*, June 1968, 16-20.

Fairly advanced discussion of molecular orbitals. Excellent use of diagrams. Recommended for the serious student of chemistry.

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and covalent compounds and with the architecture of covalent molecules. This entire book is excellent for providing information in addition to that given by the usual textbook.

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An examination of energy effects and radius ratio effects in the bonding of solids.

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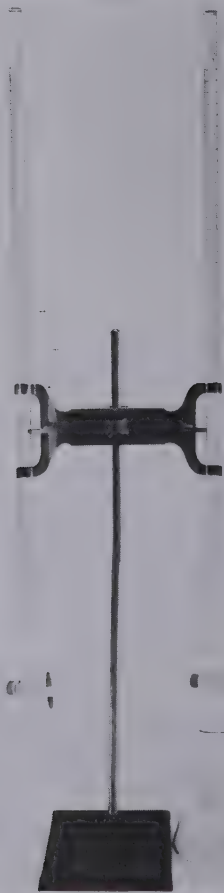
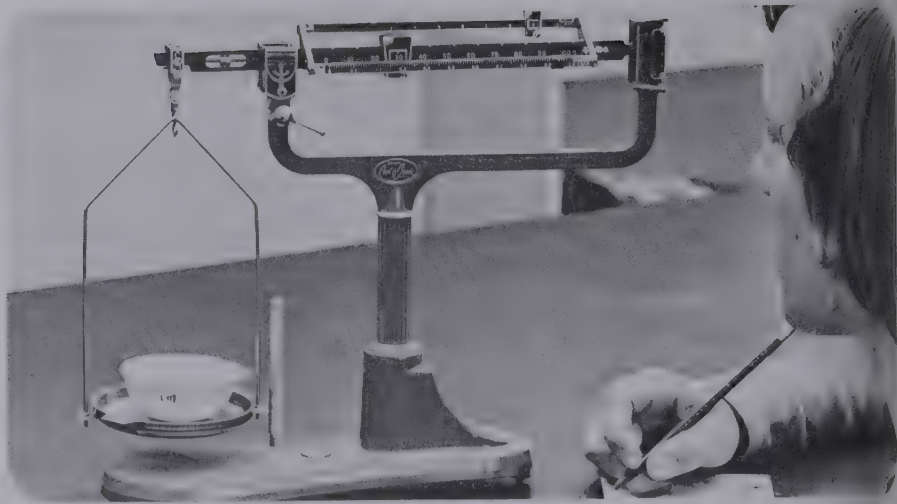
A discussion of the properties and structures of the hydrides. This article contains material that one usually has to search for in several sources.

Vaczek, Louis, *The Enjoyment of Chemistry*, The Viking Press, Inc., New York, 1964.

Chapter 10 gives a most enlightening view on how to make predictions about chemical bonds. Highly recommended.

Webb, Valerie, "Hydrogen Bond," *Chemistry*, June 1958, 16-20.

A fascinating first-person account of the importance of the hydrogen bond in relation to electronegativity. Hydrogen bonding in water, ammonia, hydrogen fluoride, and other compounds is told by hydrogen bond himself. Highly recommended for all students.





QUANTITATIVE RELATIONSHIPS IN CHEMISTRY

OBJECTIVES:

By the time you have completed your study of Chapter 8, you will be expected to demonstrate acceptable performance on the following objectives.

1. *State and apply* the accepted definitions for: molecular formula, empirical formula, subscript, coefficient, binary compound, ternary compound, mole, product, reactant.
2. *Write* the formula for a compound, given its name and a table of oxidation numbers for the ions from which the compound is made.
3. *Calculate* the molecular weight or formula weight of a compound, given its formula and a table of atomic weights.
4. *State* the name for a compound, given its formula.
5. *Interpret* a chemical equation in terms of moles.
6. *State* the type of reaction represented by an equation.
7. *Balance* a chemical equation, given the reactants and products.
8. *Determine* the number of moles present, given either a specified number of grams or a laboratory sample of matter.
9. *Calculate* the number of grams of product formed, or of reactant consumed, given sufficient other quantitative information about a reaction.

SUGGESTED ORDER OF STUDY

1. Study Secs. 8-1 through 8-4.
2. Study Secs. 8-5 and 8-6.
3. Perform Exp. 8-1. ✓
4. Study Secs. 8-7 and 8-8.
5. Perform Exp. 8-2. ✓
6. Study Secs. 8-9 through 8-11.
7. Perform Exp. 8-3. ✓
8. Perform Exp. 8-4. ✓
9. Do the Practice Exercises and review.
10. Take the Self-Test and review as necessary.
11. Take test on Chapter 8.

8-1 • ATOMIC WEIGHT



John Dalton.

Now that you have acquired some knowledge of the structure of atoms, are familiar with the periodic table, and have studied the principles of chemical bonding, you have the necessary tools for making your study of chemistry more interesting and meaningful. You will be able to write equations to express the reactions you observe and to calculate the quantities of substances used in these reactions. Perhaps you have already written equations using words. If so, you probably found these helpful in aiding your understanding of a given reaction. Chemical equations using symbols are still more useful in thinking about reactions.

You will remember from your study of Chapter 5 that one of Dalton's major contributions was his attempt to determine comparative values for the weights of atoms. He used hydrogen as a standard. By carrying out experiments, or by learning of the results of experiments that others worked on, much as you have done in your investigations, he determined other atomic weights

comparatively. Thus, he calculated that an oxygen atom was 8 times heavier than a hydrogen atom, a nitrogen atom was 4.7 times heavier, and so on.

Dalton missed on these two, oxygen and nitrogen. He thought there was probably one atom each of hydrogen and oxygen in water, that HO was the most reasonable formula for water. From this, a calculation gives comparative weights of 1 to 8. Today we have good reasons to think that the formula for water is H_2O . From this, a calculation gives comparative weights of 1 to 16. An oxygen atom is 16 times heavier than a hydrogen atom.

Dalton guessed that the formula for ammonia was NH. From this idea that ammonia has one atom each of hydrogen and nitrogen, the comparative weights can be calculated, using the results from experiments that for each gram of hydrogen in ammonia there are 4.7 g of nitrogen. So, the comparative weights are 1 for hydrogen, the standard, and 4.7 for nitrogen. According to this, a nitrogen atom is 4.7 times heavier than a hydrogen atom.

But today, we believe that in one molecule of ammonia there are three hydrogen atoms for each nitrogen atom; NH_3 is the formula. The experiments, of course, give the same results: for 1 gram of hydrogen, 4.7 grams of ammonia. But, if there are three atoms of hydrogen and only one of nitrogen, then each nitrogen atom would have to be three times heavier than Dalton thought. Today, we say that a nitrogen atom is approximately 14 times heavier than a hydrogen atom.

For many other elements Dalton's work agrees, within reasonable error, with the values we use today. For the first person to even think of comparing atomic weights, Dalton did an excellent job.

Dalton's work was extended by Berzelius, the Swedish chemist who also devised the modern system for writing chemical symbols. Berzelius was able to determine the comparative weights of atoms of about fifty elements. His results are in good agreement with those we accept today.

Today, scientists use a delicate instrument known as a mass spectrograph to determine the comparative weights of atoms with great accuracy, even being able to determine very slight differences in the weights of different atoms of the same element. Also, the standard has been changed; instead of hydrogen, the weights of atoms are compared to the most common kind of carbon atoms, called carbon-12. One mole of carbon-12 atoms weighs exactly 12.00000 grams, and the weights of all other atoms are compared to this standard.

You recall from Chapters 3 and 4 that a mole is the weight in grams represented by the symbol of an element or the formula of a compound. Thus, C for carbon represents a mole of carbon atoms. They would be mostly carbon-12 atoms since these are the most common kind of carbon atoms. So, one mole of carbon atoms represented by C weighs 12.0 grams. The atomic weight of carbon is 12.0.

The comparative weights of other atoms are compared to the standard and are called atomic weights. Thus, the atomic weight of magnesium is 24.3; from this, you can tell that a mole of magnesium atoms weighs about twice as much as a mole of carbon atoms. One magnesium atom is about twice as heavy as a carbon atom. The table of atomic weights in Appendix 12 shows the results of all the comparisons of weights of atoms. The numbers



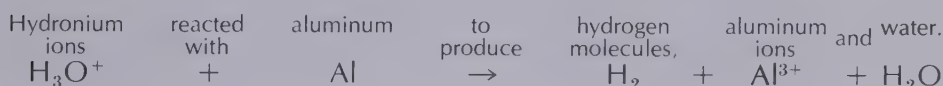
Jöns Jakob Berzelius.

in that table are the weights in grams of one mole of the atoms of the elements. A mole of atoms is a huge number of atoms; to be specific, it is 602,200,000,000,000,000. This many atoms of magnesium weigh 24.3 grams (not quite one ounce); this many atoms of oxygen weigh 16.0 grams, since the atomic weight of oxygen is 16.0.

From the numbers in the table of atomic weights, you can see that one atom of oxygen is a little heavier than one atom of nitrogen, comparing 16.0 with 14.0 grams per mole of atoms. Or, compare 12.0 grams per mole for carbon with 55.8 grams per mole of iron atoms; a single carbon atom is about one-fifth as heavy as an iron atom. A mole of zinc atoms weighs 65.4 grams, compared to 24.3 grams per mole for magnesium atoms.

8-2· HOW MANY MOLES?

In order to begin our study of quantitative chemistry, let us look more closely at the results obtained in Exp. 2-2. In this experiment you placed aluminum metal in a solution of hydrochloric acid. Hydrochloric acid is a solution of hydronium ions, H_3O^+ , and chloride ions, Cl^- . In Exp. 2-2 only the hydronium ions reacted; the chloride ions were spectators and were not involved. To express the reaction in an English sentence, and in the corresponding chemical sentence, we would say:



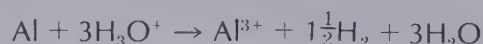
Remember that you carried out this reaction in Experiment 2-2.

Both the English sentence and the chemical sentence say the same thing, but the chemical sentence can be far more useful to a chemist because, when it is completely written, it can tell us how much reacted and how much was produced. Let's consider how to fix this chemical sentence so that it is complete.

You also observed in the experiment that all of the aluminum disappeared, or was used up. If you performed the experiment once again and used a *known* weight of aluminum and measured the amount of hydrogen gas produced, you would find that the two quantities are related. This means that quantitative observations would reveal *how many moles* of hydrogen can be produced from a known number of moles of aluminum. To make the chemical sentence complete, the numbers of moles must be included. Then the chemical sentence will be quantitative; it will express quantity in moles.

Since the symbol for an element represents one mole of atoms, we will use the symbol of aluminum, Al, to stand for one mole of aluminum atoms. Similarly, H_3O^+ stands for one mole of hydronium ions, and H_2O stands for one mole of water molecules. When this experiment is done quantitatively, we find that we can express the mole relationships in this English sentence: One mole of aluminum atoms reacts with three moles of hydronium ions (each containing three hydrogen atoms, one oxygen atom, and one positive charge), to yield one mole of aluminum ions (each with three positive charges), one and one-half moles of hydrogen molecules (each with two hydrogen atoms), and three moles of water molecules (each with two hydrogen atoms and one oxygen atom)! Notice how very complicated and involved the English sentence becomes when we attempt to tell how many moles we use and to state the composition of each substance.

See how simple it becomes to express this same reaction in a complete chemical sentence, which we call a chemical equation:



The Al stands for 1 mole of aluminum atoms and the Al^{3+} for the 1 mole of aluminum ions. When only 1 mole of a substance is involved in a reaction, the chemist does not write the "1"; it is understood. The arrow represents the words "to yield"

8-3 · CHEMICAL FORMULAS

The key in learning to write chemical equations involves the use of chemical formulas. For example, the chemical formula for water is H_2O ; the chemical formula for hydrogen molecules is H_2 . Let's look at chemical formulas in more detail.

First, a chemical formula represents a mole of units of a substance. Thus, as you know, H_2O signifies a mole of water molecules. If we wish to signify some other number of molecules in a chemical equation, say half a mole, we write $\frac{1}{2}\text{H}_2\text{O}$, or $0.5\text{H}_2\text{O}$; to specify 3.6 moles, for example, we write $3.6\text{H}_2\text{O}$.

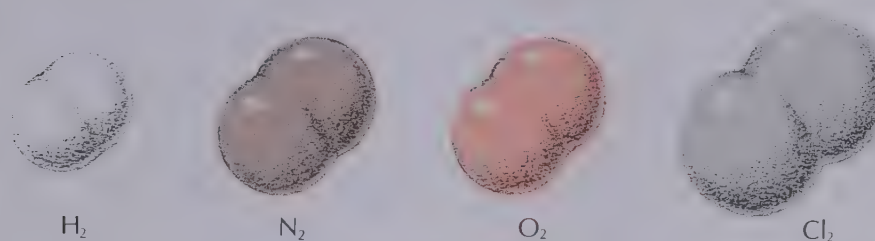
Second, a chemical formula represents the composition of a substance. When we write H_2O , we specify two atoms of hydrogen and one atom of oxygen in each molecule of water. (The subscript 1 for the oxygen symbol



H_2O

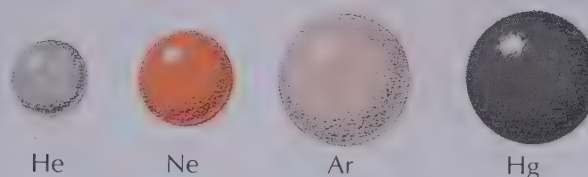
is understood, so although we could write H_2O_1 for water, we do not need to do so; H_2O is satisfactory.)

As long ago as 1811, Avogadro discovered evidence that molecules of some gaseous elements, such as hydrogen, chlorine, and oxygen, contained two atoms in each molecule. So the chemical formula for hydrogen molecules is H_2 , for chlorine Cl_2 and, of course, O_2 for oxygen.



The symbol N_2 , then, represents one mole of nitrogen molecules, each with two atoms of nitrogen, weighing 28.0 grams. The table of atomic weights lists the weight of a mole of nitrogen atoms as 14.0 grams, so a mole of double-atom nitrogen molecules would weigh twice as much.

Today, we know that some gas molecules are monatomic, such as those of the noble gases, which are in Group VIIIA in the periodic table. Thus, a mole of helium molecules is the same as a mole of helium atoms, since this gas has only one atom in its molecule; the symbol is He for a mole of helium molecules. The same applies to neon, Ne; argon, Ar; and all the others in this group. Other elements exist as monatomic molecules in the gaseous state. Mercury, Hg, is an example.



Only eight elements have diatomic molecules: *hydrogen, oxygen, nitrogen, and the halogens* of Group VIIA in the periodic table: fluorine, chlorine, bromine, iodine, and astatine. In the gaseous state, each molecule consists of two atoms which bond by sharing a pair of electrons. A non-polar covalent bond is formed between the two atoms.

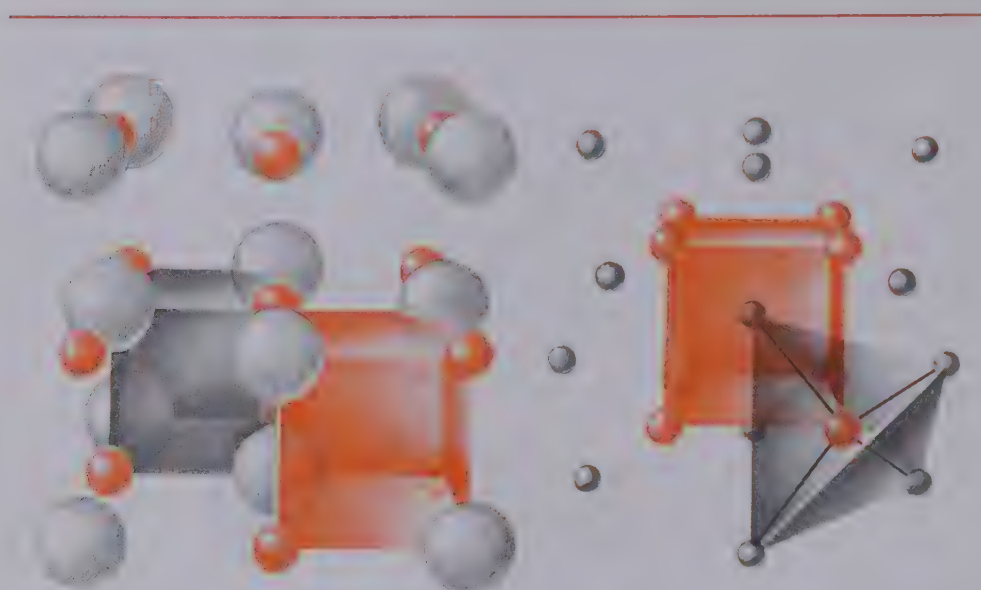
Formulas for Ionic Compounds

When electrons are shared, the bond is either covalent or polar covalent and molecules are formed. We can speak of *molecular formulas*. Examples are H_2O , one mole of water molecules, and N_2 , representing one mole of nitrogen molecules. If there is no bonding at all, but single atoms, these are called molecules also, such as Ar for a mole of argon molecules.

When ions are present, the formula is called an *empirical formula*. An example is KCl. It is not possible by merely looking at a chemical formula, such as KCl or H_2O or CO_2 , to tell whether it is an empirical formula or a molecular formula. One, KCl, is an empirical formula for the ionic compound potassium chloride. The other two are molecular formulas for water, H_2O , and

carbon dioxide, CO_2 . The way to tell is to compare electronegativities of the elements within the compound. Ionic compounds can be expected when the difference in electronegativities of the two elements is about 1.8 or more. Potassium chloride is a good example. From the listing of electronegativities in Chapter 7, you can note that the electronegativity of potassium, K, is 0.8 and that of chlorine, Cl, is 3.0, so the difference is 2.2.

Empirical formulas for ionic compounds represent a mole of each of the ions. For example, KCl does not represent a mole of molecules but, instead, a mole of potassium ions and a mole of chloride ions. Or, we could say, the symbol KCl represents a mole of ion pairs, potassium and chloride. Calcium fluoride is an ionic compound with the empirical formula CaF_2 . This would represent a mole of calcium ions and two moles of fluoride ions.



Models for the crystal lattices of two ionic compounds, sodium chloride (NaCl) and calcium fluoride (CaF_2).

In ionic compounds each particle is an ion. Sometimes one ion has a single positive charge, sometimes a double or even a triple positive charge. Sometimes the other ion has a single, double, or higher negative charge. The charge carried by ions composed of single atoms can be predicted from the periodic table. For convenience the following generalizations will aid you in predicting the ionic charge of the elements:

1. In Groups IA, IIA, and IIIA, the atoms can be expected to lose their outer energy level electrons. If this happens, then the charge acquired by ions in these groups is $1+$, $2+$, and $3+$, respectively.
2. Elements in Groups VIA and VIIA are generally nonmetallic, and their atoms tend to take electrons to form ionic bonds if the electronegativity difference is large enough. When this happens, the charges acquired by the ions are $2-$ and $1-$, respectively.

8-4 · SUGGESTIONS FOR WRITING CHEMICAL FORMULAS CONTAINING TWO ELEMENTS

The formula for a substance can be determined only by laboratory measurement in experiments designed to yield the necessary data. As a result of hundreds of thousands of such investigations, a set of *oxidation number rules* has been compiled that enable us to predict the formula that can be determined by experimentation.

The electron configuration of an atom determines the number of electrons it will lose, gain, or share in bonding with another atom (or ion) to give it the configuration of its nearest noble gas neighbor. The *oxidation number is defined as the charge which the atom acquires, or appears to acquire, upon bonding with another atom.*

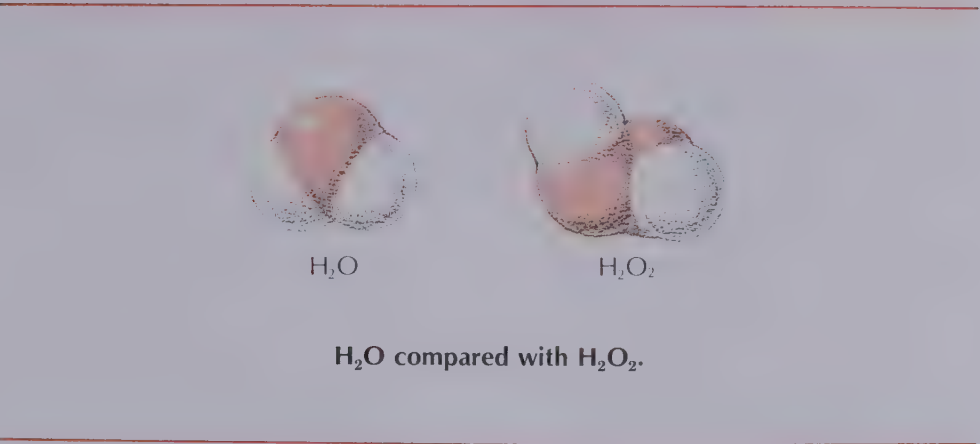
You can use the rules to write correct chemical formulas for covalent and ionic compounds containing two elements. The oxidation number rules given here are correct, but incomplete. You will be given other rules as they are needed.

Oxidation Number Rules for Writing Formulas Containing Two Elements

1. Locate the symbols of the elements in the compound in the periodic table listing oxidation numbers. Determine the oxidation number of each element from the table. Oxidation numbers in parentheses are not commonly used.
2. Always write the symbol of the element with the *positive* oxidation number *first*. Follow this with the symbol of the element with the negative oxidation number.
3. In compounds the *sum* of the oxidation numbers must be zero. That is, the total positive (+) oxidation number must equal the total negative (−) oxidation number. Adjust the + or − values by using *subscripts*. A subscript is a number written at the lower right of a symbol. The subscript must not be changed, once it is written so that the sum of the oxidation numbers is zero.

Let us try some examples. Write the chemical formula for the compound that is composed of the elements sodium and iodine. Sodium, Na, is in Group IA; it has an oxidation number of +1, as you can see from the information at the bottom of the Group IA column. Iodine, I, is in Group VIIA. So it has one of these oxidation numbers: −1, +5 or +7. The −1 is not in parentheses; the +5 and +7 are enclosed in parentheses. This is intended to signify that −1 is more common and the other two are not as common for our work. Therefore, the formula is NaI, because +1 and −1 add to zero.

What is the formula for the compound consisting of calcium and fluorine? Calcium, Ca, is in Group IIA, and fluorine, F, is in group VIIA. The formula is CaF_2 ; we need two as a subscript on the F symbol to make two −1's, since the oxidation number of calcium is +2. Then, +2, −1, and −1 add to zero. It would be wrong to change the subscripts and write CaF_3 , or Ca_2F_5 , for example.



Try for the formula of the compound containing hydrogen and oxygen. Hydrogen, H, is by itself, above Group IA, and oxygen, O, is in Group VIA. Using the +1 for hydrogen and the −2 for oxygen, we get H₂O, which we know is the formula of water. There is another compound of hydrogen and oxygen possible, using the +1 for hydrogen and the −1 for oxygen. This gives us HO as the formula for hydrogen peroxide. However, it is known from other laboratory work that a mole of gaseous hydrogen peroxide molecules weighs about 34 grams. This number of grams can be accounted for by assuming that the molecular formula for hydrogen peroxide is H₂O₂. With +1 for hydrogen and −1 for oxygen, this still adds to zero, as +1 +1 −1 −1 = 0.

What is the chemical formula for the compound containing tin, Sn, in Group IVA, and chlorine, Cl, in Group VIIA? Since the oxidation number for tin is +2 or +4 and we cannot tell that one is more or less commonly used than the other, we have two possible answers, SnCl₂ and SnCl₄, since we can identify −1 as the oxidation number to be used for chlorine.

These three rules will work for compounds that contain only two elements. More rules are needed for compounds that contain more than two elements, as we will learn later in this chapter.

Summary of Examples Discussed in Secs. 8-4 and 8-5							
Elements Combining	Element with + Oxidation No.			Element with − Oxidation No.			Formula
	Symbol	Group	Oxidation Number	Symbol	Group	Oxidation Number	
sodium, iodine	Na	IA	+1	I	VIIA	−1	NaI
calcium, fluorine	Ca	IIA	+2	F	VIIA	−1	CaF ₂
hydrogen, oxygen	H	IA	+1	O	VIA	−2	H ₂ O
tin, chlorine	Sn	IVA	+2 or +4	Cl	VIIA	−1	SnCl ₂ SnCl ₄
sulfur, oxygen	S	VIA	−2, +4, or +6	O	VIA	−2 (−1)	SO ₂ SO ₃

Table 8-2

8-5. NAMING COMPOUNDS THAT CONTAIN ONLY TWO ELEMENTS (Binary Compounds)

Name the element with the positive oxidation number first, and the element with the negative oxidation number second, but put an *-ide* ending on the name of the element with the negative oxidation number.

For example, NaCl is not sodium chlorine; it is called sodium chloride. CaF_2 is called calcium fluoride. SnCl_2 and SnCl_4 both have the same name, tin chloride.

To prevent confusion, when you wish to talk about only one of the two tin chlorides, the oxidation number of the element with the positive oxidation number, tin, is given in Roman numerals, in parentheses, like this: SnCl_2 is tin(II) chloride, and SnCl_4 is tin(IV) chloride. On some bottles of tin chloride, you will see the name stannous chloride, for SnCl_2 , and stannic chloride, for SnCl_4 . These are the old, classical names for these two compounds of tin and chlorine; *-ous* indicates the lower oxidation number and *-ic* indicates the higher oxidation number.

Iron, Fe, has two oxidation numbers, +2 and +3. What are the formulas and names for the compounds containing only iron and oxygen? Using the more common oxidation number for oxygen, -2 , we get FeO , iron(II) oxide; and Fe_2O_3 , iron(III) oxide.

What are the names and formulas for compounds of sulfur and oxygen? Again, oxygen has an oxidation number of -2 (because this is the most common), and sulfur will necessarily have an oxidation number of +4 or +6 (it cannot be negative also, since the oxygen is negative), and we cannot tell which, so there are two compounds, SO_2 and SO_3 . To name these, we could say sulfur(IV) oxide and sulfur(VI) oxide. However, when the element with a positive oxidation number is a nonmetal, most chemists prefer to become Greeks and use Greek prefixes indicating the number of moles of each ion instead of Roman numerals indicating the oxidation number. Here are the Greek number prefixes from one to five:

Prefix	Number
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5

So, SO_2 is called monosulfur dioxide, and SO_3 is called monosulfur trioxide. Often, to save time and trouble, the *mono-* prefix is omitted for the element with the positive oxidation number. Therefore, the easy, correct names are sulfur dioxide for SO_2 and sulfur trioxide for SO_3 . It is correct to use these Greek prefixes for any compounds, if you wish. You can say tin tetrachloride for SnCl_4 , or di-iron trioxide for Fe_2O_3 , for examples. However, you would not omit both *mono*-s for FeO ; it is iron monoxide, not iron oxide. Notice that we use either Greek prefixes or Roman numerals only when an element has more than one possible oxidation number. This information is summarized in Table 8-3.

Some Common Binary Compounds		
Formula	Modern names	Classical names
SO ₂	<i>sulfur dioxide</i> sulfur(IV) oxide	sulfur dioxide
SO ₃	<i>sulfur trioxide</i> sulfur(VI) oxide	sulfur trioxide
SnCl ₂	<i>tin(II) chloride</i> tin dichloride	stannous chloride
SnCl ₄	<i>tin(IV) chloride</i> tin tetrachloride	stannic chloride
FeO	<i>iron(II) oxide</i> iron monoxide	ferrous oxide
Fe ₂ O ₃	<i>iron(III) oxide</i> di-iron trioxide	ferric oxide
MgO	magnesium oxide	magnesium oxide
KBr	potassium bromide	potassium bromide
CaF ₂	calcium fluoride	calcium fluoride
N ₂ O	<i>dinitrogen monoxide</i> dinitrogen oxide	nitrous oxide
NO	nitrogen monoxide	nitric oxide

Note: Where two names are given, the preferred name is italicized.

Table 8-3

8-6 • NAMING COMPOUNDS THAT CONTAIN MORE THAN TWO ELEMENTS (Ternary Compounds)

In Exp. 3-1 you placed a large blue crystal of copper sulfate in each of two vials of water in order to study an equilibrium involving a solid and a liquid. Copper sulfate contains three elements: copper, sulfur, and oxygen. Sodium hydroxide is another compound you have used several times in your laboratory work. It contains three elements: sodium, hydrogen, and oxygen.

In order to understand how such compounds are named and how their formulas are written, look at Table 8-4, which lists some ions and their charges.

There are other ions, but these are enough to consider now. The charge on each ion is the same as the oxidation number of the ion; this makes figuring it easy. As before, the positive part is named first, the negative part is named second. What is the name of NH₄Cl? The name for the part with the positive oxidation number is “ammonium”; the negative part is an element, so make the ending “ide,” and we get ammonium chloride. Similarly, NH₄I would be ammonium iodide. Notice that, as usual, the oxidation numbers add to zero: +1 (for NH₄⁺) and −1 (for I) equal zero.

All the other ions of interest to us have negative oxidation numbers; since these are not elements, but combinations of elements, they keep their name when they are in a compound. What is the name of NaHCO₃? This name

Some Common Ions	
Name of Ion	Formula of Ion, and Charge
Ammonium	NH_4^+
Carbonate	CO_3^{2-}
Hydrogen carbonate	HCO_3^-
Hydroxide	OH^-
Nitrate	NO_3^-
Nitrite	NO_2^-
Phosphate	PO_4^{3-}
Sulfate	SO_4^{2-}
Sulfite	SO_3^{2-}
Acetate	$\text{C}_2\text{H}_3\text{O}_2^-$

Table 8-4

is sodium hydrogen carbonate; another name for it is "baking soda." What is the name for CaCO_3 ? It is calcium carbonate.

What is the name for NaNO_3 ? Sodium nitrate. Lead(II) nitrate is $\text{Pb}(\text{NO}_3)_2$. Before, we have called this compound lead nitrate. You can see that it is necessary to identify the oxidation number of the lead; otherwise, you could not tell whether we had the other lead and nitrate compound in mind, with an oxidation number of +4 for the lead, $\text{Pb}(\text{NO}_3)_4$.

Notice that the nitrate ion, NO_3^- , has an oxidation number of -1 , and that we therefore need two of these ions to balance off the $+2$ oxidation number of the lead. To express this correctly, the symbol for the ion is put inside parentheses, (NO_3) , and the subscript, 2, is put outside the parentheses, on the lower right, $(\text{NO}_3)_2$. Then, the correct formula is written as $\text{Pb}(\text{NO}_3)_2$.

What is the correct formula for calcium hydrogen carbonate? Since the hydrogen carbonate ion has an oxidation number of -1 and the calcium itself has an oxidation number of $+2$, we need two hydrogen carbonate ions. Therefore, we write $\text{Ca}(\text{HCO}_3)_2$.

Let us now summarize these rules for compounds containing more than two elements:

1. Identify the oxidation numbers of the elements or ions in the compound.
2. Write the symbol for the positive component first, then the symbol for the negative component.
3. Write subscripts, or parentheses and subscripts if necessary, to make the sum of all the oxidation numbers add to zero.
4. To name the compound, state the name of the component, the ion or element, with the positive oxidation number first. Then state the name of the component with the negative oxidation number. If that one is an element, change the ending to "ide." If it is a complex ion, keep the name as it is.
5. Where there is possible doubt about the positive oxidation number of the element, such as iron or tin or sulfur or carbon or nitrogen, use Roman numerals in parentheses to specify the oxidation number or Greek prefixes to specify the number of moles, whichever you wish.

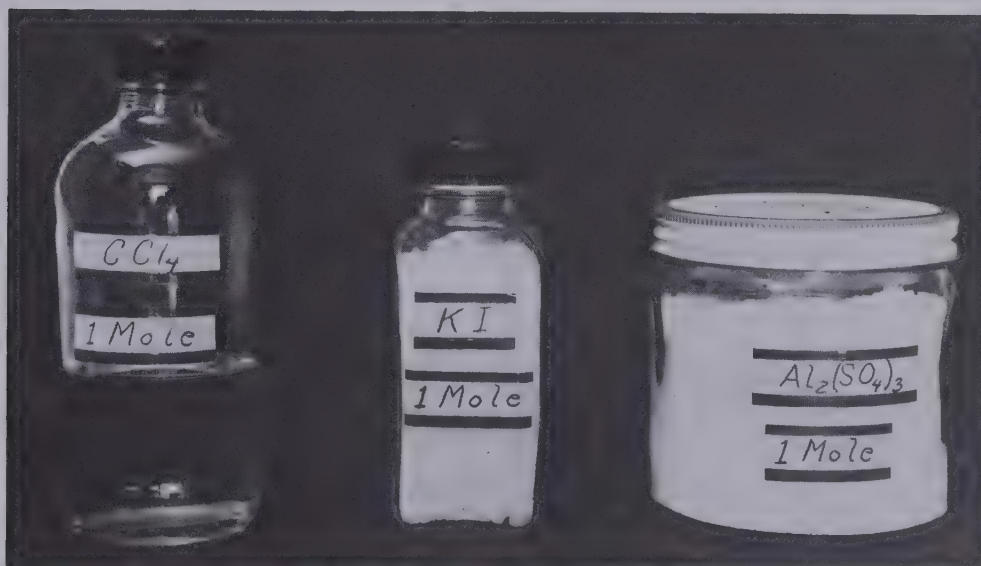
8-7. FORMULAS INDICATE THE WEIGHT OF A MOLE

What is the weight of a mole of carbon tetrachloride molecules? From the name, we can tell that the formula is CCl_4 . The formula stands for a mole of molecules. It also represents one mole of carbon atoms and four moles of chlorine atoms. From this, we can figure out the weight of a mole of these molecules.

In the table of atomic weights we can see that the weight of a mole of carbon atoms is 12.0 grams (to three significant figures), and the weight of four moles of chlorine atoms is 4×35.5 grams, or 142 grams, to three significant figures. Adding 12.0 grams and 142 grams, we get 154 grams as the weight of a mole of carbon tetrachloride molecules.

What is the weight of a mole of potassium iodide units (ion pairs)? Potassium iodide is an ionic compound, and does not consist of molecules; its empirical formula is KI , as we know. A mole of these ion pairs consists of a mole of potassium ions, which weigh 39.1 grams, according to the table of atomic weights. (A potassium ion is a potassium atom which has lost one electron, and that electron is so light that even for a mole of particles, the weight is the same to four or even more significant figures.) A mole of iodide ions weighs 126.9 grams. Therefore, by adding 126.9 grams and 39.1 grams, we get 166.0 grams as the weight of a mole of potassium iodide ion pairs. Sometimes, to shorten this, we say that the *formula weight* of potassium iodide is 166.0 grams per mole.

We can say the same thing for molecules, such as carbon tetrachloride. The *molecular weight* of carbon tetrachloride is 154 grams per mole. Formula weight applies to ionic compounds, molecular weight to covalent and polar covalent molecules, and either one is determined by adding the weights of the atoms, or ions, per mole to get the total number in grams. Keep track of the number of moles, of course. For CCl_4 one mole of carbon atoms and four moles of chlorine atoms are to be added. One mole each of potassium and iodine are to be added in the case of potassium iodide.



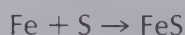
Here is an example that illustrates the need to keep track of the number of moles very carefully. What is the formula weight of the ionic compound aluminum sulfate? To answer this, we must first figure out its formula. Aluminum has an oxidation number of +3, as we can see from the periodic table listing of oxidation numbers; sulfate ion has an oxidation number of -2 from the list in Table 8-4. Therefore, aluminum sulfate has a formula expressed as two aluminums and three sulfates, with parentheses around the sulfate ion symbol: $\text{Al}_2(\text{SO}_4)_3$.

To figure out the formula weight, we need to know the weight of two moles of aluminum atoms, which is 2×27.0 grams. We also need to know the weight of three moles of sulfate ions. Since each sulfate symbol represents one mole of sulfur atoms and we have three such in aluminum sulfate, this is 3×32.1 grams. Finally, we need the weight of twelve moles of oxygen atoms (four in each sulfate, times three). This is 12×16.0 grams. We calculate as follows:

Aluminum	$2 \times 27.0 \text{ g} = 54.0 \text{ g}$
Sulfur	$3 \times 32.1 \text{ g} = 96.3 \text{ g}$
Oxygen	$12 \times 16.0 \text{ g} = \underline{192.0 \text{ g}}$
	342.3 grams, the formula weight of aluminum sulfate.

8-8. CHEMICAL SENTENCES AND CHEMICAL EQUATIONS

Now we can apply what you have learned to extend the ideas even farther. In Exp. 2-4 you observed a reaction of sulfur and iron. The product formed was iron(II) sulfide, FeS . The chemical sentence for this reaction can be written:



This sentence is complete, so it also is a chemical equation. That is, the number of moles of iron atoms on the left of the arrow is the same as on the right, one mole. The same is true for the number of moles of sulfur on the left and right.



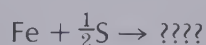
Again, remember that you carried out this reaction in Experiment 2-4.

In English, the chemical equation states that one mole of iron reacts with one mole of sulfur to yield one mole of iron(II) sulfide. From the table of atomic weights, we can learn that one mole of iron atoms weighs 55.8 grams and one mole of sulfur atoms weighs 32.1 grams. So, in English, the chemical equation also states that 55.8 grams of iron reacts with 32.1 grams of sulfur to yield 87.9 grams of iron(II) sulfide. This is a quantitative statement; it states how much.

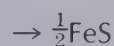
It tells us even more. Suppose that we mixed 100 grams of iron with 32.1 grams of sulfur. Would all the iron react? No, about 44 grams would be left over; only 55.8 grams would react.

Or, if we had 55.8 grams of iron and, say, 50 grams of sulfur, about 18 grams of sulfur would be left over after the reaction.

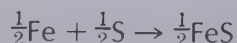
Suppose that we had half a mole of sulfur, say 16 grams (rounded off). How much iron would react? To find out, it is best to write a new chemical equation first, like this to start, with only half a mole of sulfur symbolized:



With only half a mole of sulfur, we can obtain only half a mole of iron(II) sulfide:

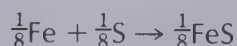


And half a mole of iron sulfide would need only half a mole of iron. This is our new chemical equation:



The equation shows that only half a mole of iron is needed to react with half a mole of sulfur. Since one mole of iron weighs 56 grams, half a mole weighs 28 grams. Therefore, if we had 16 grams of sulfur, it would react with 28 grams of iron to yield 16 grams + 28 grams, or 44 grams, of iron(II) sulfide.

In Exp. 2-4 you used 4 grams of sulfur, or about one-eighth of a mole of sulfur. (One mole of sulfur weighs 32.1 grams, so 4 grams is one-eighth of a mole of sulfur, almost exactly.) This is the complete chemical equation:



Since one mole of iron weighs 55.8 grams, one-eighth mole will weigh $\frac{1}{8} \times 55.8$ g, or about 7 g. Perhaps you recall that the directions for Exp. 2-4 specified 4 grams of sulfur and 7 grams of iron. This is how those numbers were figured out. First, it was decided that 4 grams of sulfur would be about enough, and then the necessary amount of iron was calculated.

Problem:

In Exp. 2-4, how many grams of iron(II) sulfide were formed?

8-9. CHEMICAL EQUATIONS AND PROBLEM SOLVING

To continue, it will be helpful to examine other applications of chemical equations. But first, we will summarize the ideas from Sec. 8-8 and add more detail, as well.

In order to write a correct chemical equation, we must know:

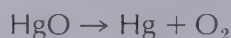
1. That the reaction can actually occur in the laboratory. Being able to write a chemical equation for a reaction on paper does not guarantee that the reaction can actually take place.
2. The correct chemical formulas for the *reactants*, on the left side of the arrow, and the correct chemical formulas for the *products*, on the right side. Sometimes these will be molecular formulas, sometimes empirical. But always, they are written with the correct subscripts as determined from our knowledge of oxidation numbers. Once the formula is correctly written, these subscripts are never changed.
3. How to write a chemical sentence describing what happens, using plus signs and an arrow to represent the reactants on the left which form, or yield, the products on the right of the arrow.
4. That it is necessary to balance the numbers of moles, so that the same number of moles of each element are shown on the left and right. (In our example with iron, sulfur, and iron(II) sulfide, we used fractions; whole numbers and decimals can be used, also.) The fractions or whole numbers or decimal numbers used to balance the number of moles are called *coefficients*. So, this step can be stated briefly: It is necessary to balance by using coefficients; if no coefficient is expressed, it is understood to be 1, for one mole. Coefficients can be changed, but if one is changed, the others must also be changed.

In order to solve a problem, we must carry out these steps:

5. Write a correct chemical equation, that is, one with balanced numbers of moles, for a reaction that will take place in the laboratory. (This requires the application of steps 1 through 4, above.)
6. From the number of grams of a substance stated in the problem, figure out the fraction or decimal amount of a mole involved for the given substance. (Or, if a larger quantity of given substance is stated in the problem, figure out how many moles of it are involved.)
7. Adjust the numbers of moles for all the other substances in the equation, writing a new chemical equation with a different set of coefficients, making sure that all elements are balanced.
8. From the new number of moles of one of the other substances, calculate the amount in grams of the substance asked for in the problem.

Let us use some examples from Exp. 8-3 to illustrate these steps. When mercury(II) oxide is heated, molecular oxygen and mercury metal are formed. There is only one reactant, mercury(II) oxide; its formula is HgO , as we can tell by using information about oxidation numbers. The formulas of the products are Hg , metallic mercury, and O_2 , molecular oxygen.

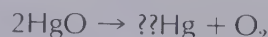
Here is the correct, but incomplete, chemical sentence:



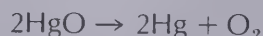
To make this sentence complete, to convert it to a chemical equation, we notice that one mole of oxygen atoms is symbolized on the left and two moles of oxygen atoms are symbolized on the right. That is, one mole of oxygen

molecules is symbolized on the right, and each oxygen molecule is composed of two oxygen atoms.

To balance the oxygen, we can add the coefficient 2 to the HgO:

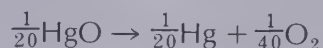


But now the Hg mole symbols are unbalanced. To bring them into balance, we need to add another coefficient, 2, to the Hg symbol on the right of the arrow:



Now we have a chemical equation. We are ready for the problem. Some mercury(II) oxide was heated and 10 grams of mercury were produced; how many grams of oxygen were also produced? From the table of atomic weights, we can find that one mole of mercury weighs 200.6 grams. To make our problem simpler to think about, we shall round this off to 200 grams. If one mole of mercury atoms weighs 200 grams, then 10 grams would be one-twentieth mole of atoms.

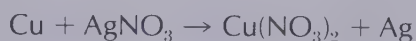
The chemical equation tells us that we get half as many moles of oxygen molecules as we get moles of mercury atoms. For every two moles of mercury atoms, we get only one mole of oxygen molecules. So, if we get one-twentieth mole of mercury atoms, we will also get one-half of one-twentieth, or one-fortieth, mole of oxygen molecules. Here is the new chemical equation which tells us this, in symbols:



How much would this oxygen weigh? One mole of oxygen molecules weighs 32.0 grams. (One mole of oxygen atoms weighs 16.0 grams, according to the table of atomic weights, and there are two moles of atoms in one mole of oxygen molecules.) So, we will obtain one-fortieth of 32.0 g of molecular oxygen, that is, $\frac{1}{40} \times 32$ g, or $\frac{1}{5}$ gram. In decimals, this equals 0.8 gram of molecular oxygen. This is the answer to our problem.

Problems

1. a. When you placed a piece of copper metal in a solution of silver nitrate, a blue solution of copper(II) nitrate was formed, and silver metal also was produced. The chemical sentence is:



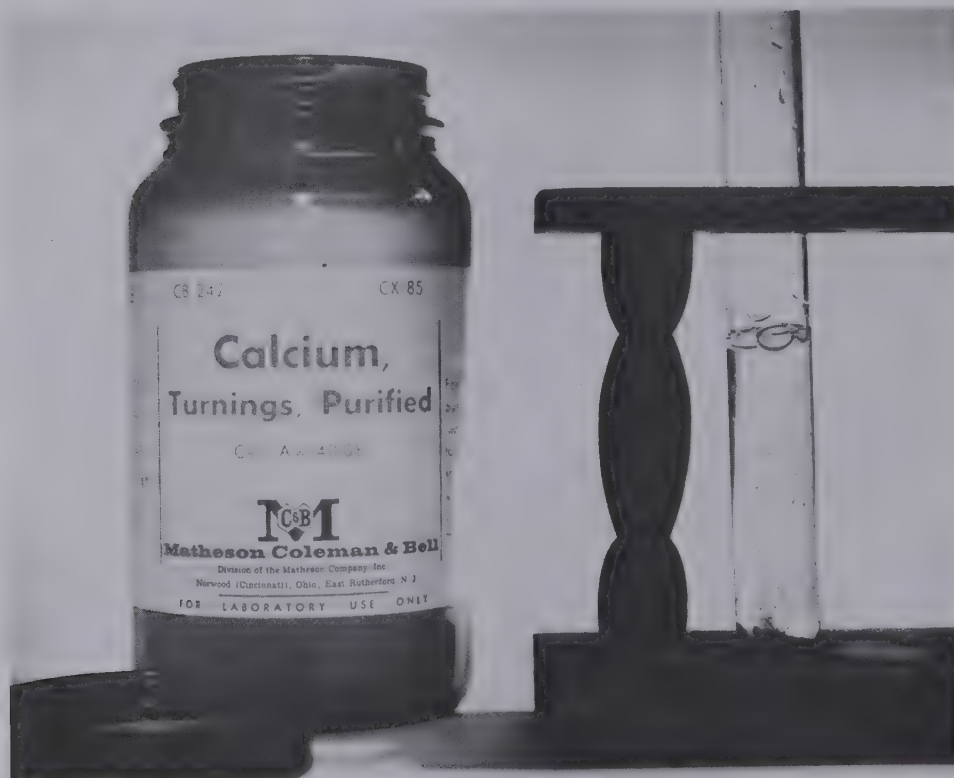
Convert this into a chemical equation.

- b. How many grams of silver can be produced when 21 grams of copper are put into a large beaker containing plenty of dissolved silver nitrate? To make this problem a little easier, round off the weight of one mole of copper from 63.5 to 63 grams.
2. In your study of combination reactions, magnesium reacted (mostly) with the oxygen in the air to form magnesium oxide. How many grams of magnesium oxide could be formed by burning 3 grams of magnesium?



What is the equation for the reaction between copper metal and silver nitrate solution?

3. It has been found in the laboratory that calcium metal will react with water to produce molecular hydrogen and calcium hydroxide. How many grams of calcium and how many grams of water are consumed if 4 grams of hydrogen are produced?



What is the equation for the reaction of calcium metal with water?

8-10. TYPES OF CHEMICAL REACTIONS

There are many different types of chemical reactions; synthesis, decomposition, oxidation-reduction, acid-base are examples. In this chapter we have seen several of these. Let us classify the reactions studied in this chapter and round out our knowledge further. You should be able to write chemical equations for each example given.

Synthesis reactions

In synthesis reactions, elements react to produce compounds. Aluminum reacts with oxygen in the air to form aluminum oxide. Magnesium reacts with the oxygen in the air to form magnesium oxide. Magnesium will also react with nitrogen in the air to form magnesium nitride. (Actually, when you burn magnesium in air, most of it reacts to form magnesium oxide; only a little forms magnesium nitride, Mg_3N_2 .) Magnesium nitride is a green solid. It reacts with water to form ammonia, NH_3 , and magnesium oxide.

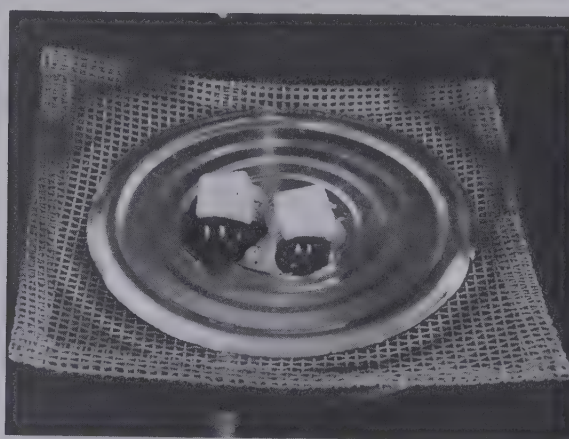
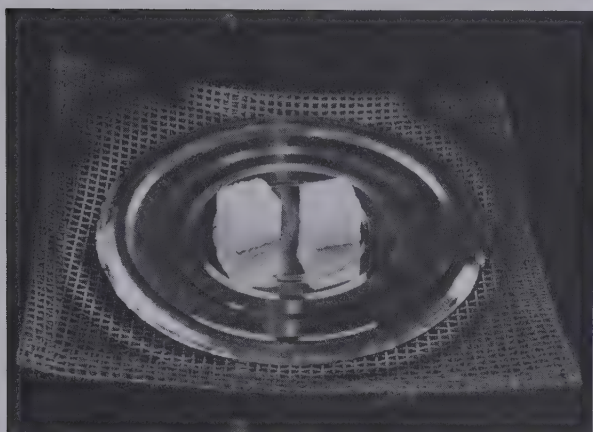
Decomposition reactions

Mercury(II) oxide decomposes into mercury and molecular oxygen when

heat energy is supplied. Water decomposes into molecular hydrogen and molecular oxygen when heat energy is supplied at high temperatures or when electrical energy is supplied at lower temperatures.

Rearrangement, or changed-combination, reactions

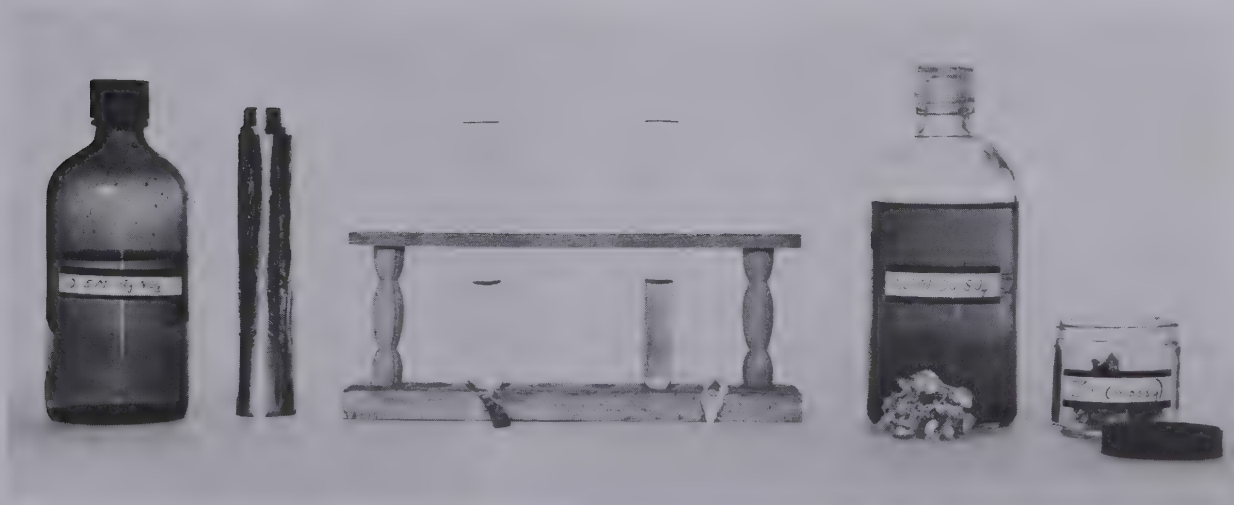
In this type of reaction, two compounds react in such a way as to produce two new compounds. For example, magnesium nitride, Mg_3N_2 , reacts with water to produce ammonia, NH_3 , and magnesium oxide, MgO .



What kind of reaction is the sugar undergoing?

Metal-ion reactions

Copper metal reacts with ionized silver nitrate in solution to form copper ions and silver metal while the nitrate ions remain, as spectators. When zinc metal reacts with an ionic solution of copper(II) sulfate, zinc ions and copper metal are produced; the sulfate ions are spectators. Mercury(II) ions react with aluminum metal; chloride ions are spectators.



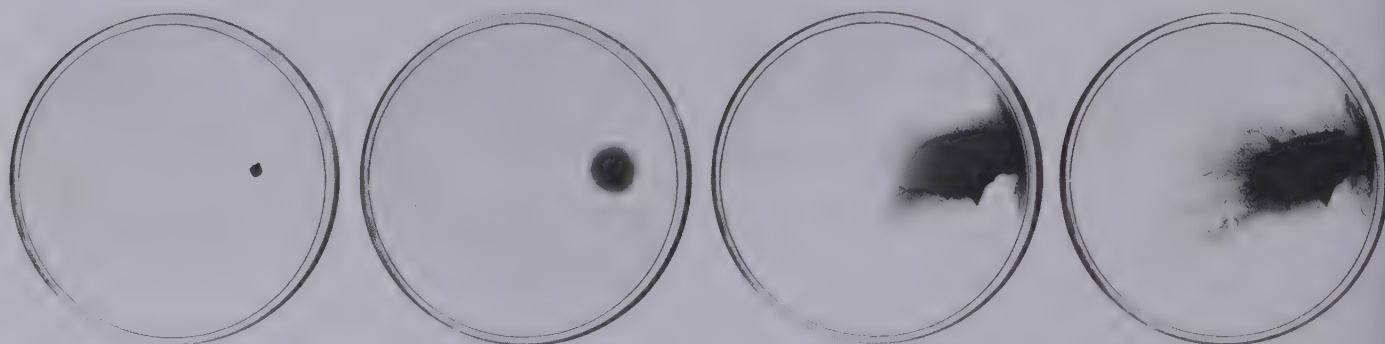
Apply your knowledge of chemical equations as you do Experiment 8-3.

Ion-ion reactions

Lead(II) ions and nitrate ions, in one solution, will react with potassium ions and iodide ions, in another solution, when the two solutions are mixed. Lead (II) iodide precipitates; the other ions are spectators.



Apply your understanding of this section in your performance of Experiment 8-4.



The petri dish initially contained distilled water, crystals of sodium thiosulfate, and potassium permanganate. What has happened in this little chemical system?

Problem

Select two or three reactions from your laboratory work with other experiments and write the chemical equations which describe the reactions that you observed. Classify the reactions you select.

8-11 • PREVIEW AS INCENTIVE TO REVIEW

You may have felt that this was a difficult chapter; we have emphasized the importance of quantitative work. Your own laboratory work should be as quantitative as possible. If you are to make it really quantitative, then you

need to master the skills of formula writing and equation writing, plus the arithmetic needed to convert moles to grams and grams to moles. These skills are not difficult, but they do require practice and careful calculations. Mastery of these skills distinguishes the committed chemistry student from the uncommitted. We think it is worth your time to master these skills. We hope you will give it a try.

Coming up soon, after a few more chapters, is a part of chemistry that most people think is very enjoyable. You will be applying your knowledge to the solution of a mystery. The quantitative study in this chapter and the less difficult material in the next two chapters form part of the necessary background, if you hope to be able to enjoy the mystery chapter. The questions to be solved then involve finding out by detective-like work, with logical thinking, what unknown substance is present in a solution. Often, in real detective work the same kind of logical thinking that you will do then is carried out to solve crimes, to figure out the causes of airplane crashes, to find the sources of pollution, and to make both our lives and this world better by applying chemical knowledge.

Practice Exercises *(Answers on pp. 318, 319)*

- Write formulas for the following compounds:
 - iron(II) sulfate
 - lead(II) nitrate
 - carbon disulfide
 - manganese dioxide
 - sulfur trioxide
- State the names of the following compounds:
 - $\text{Cu}(\text{NO}_3)_2$
 - HgCl_2
 - CaO
 - Mn_2O_5
 - N_2O
- Calculate the molecular or formula weights of the following substances:
 - KClO_3
 - $\text{Al}(\text{NO}_3)_3$
 - Na_2SO_4
 - AgCl
 - KMnO_4
- Given: $3\text{Ag} + 4\text{HNO}_3 \rightarrow 3\text{AgNO}_3 + \text{NO} + 2\text{H}_2\text{O}$.
 - How many moles of HNO_3 are used to produce 1 mole of NO ?
 - How many grams of HNO_3 are used?
 - How many moles of water are produced?
 - How many atoms are contained in each molecule of the product, NO ?
- Given: $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$.
 - How many moles of calcium are used to produce 1 mole of each product?
 - What weight of calcium must be used to produce 1 mole of each product?
 - If 4 grams of Ca are used, how many moles of $\text{Ca}(\text{OH})_2$ will be produced?
 - How many grams of $\text{Ca}(\text{OH})_2$ were produced in step c?
- Balance the following chemical sentences:
 - $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$
 - $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$
 - $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4$
 - $\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$
 - $\text{Al}_2(\text{SO}_4)_3 + \text{NaHCO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{Al}(\text{OH})_3 + \text{CO}_2$

7. Classify the following reactions as to type:
- $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$
 - $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$
 - $\text{Cl}_2 + 2\text{NaI} \rightarrow 2\text{NaCl} + \text{I}_2$
 - $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$
 - $2\text{NaOH} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
8. Given: $\text{Cu} + 2\text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$
- How many moles of silver could be produced in this reaction if 12.7 g of copper metal is used?
 - How many grams of silver would be produced in the reaction?
9. Given: $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$
- In the above reaction, 0.40 gram of hydrogen was produced. How many moles is this?
 - How many moles of zinc were required to produce that quantity of hydrogen?
 - How many grams of zinc were required?
10. Given: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
- If 159.0 grams of CaCO_3 are used in the above reaction, how many moles is this?
 - How many moles of CO_2 would be produced by heating 159.0 grams of CaCO_3 ?
 - How many grams of CO_2 would be produced?
11. (Multiple Completion; see special directions in Appendix 13)
The formula for SO_2 (molecular weight, 64.1) represents
- one mole of the compound
 - 64.1 grams of the compound
 - one molecule of the compound
 - one mole of sulfur atoms and two moles of oxygen atoms

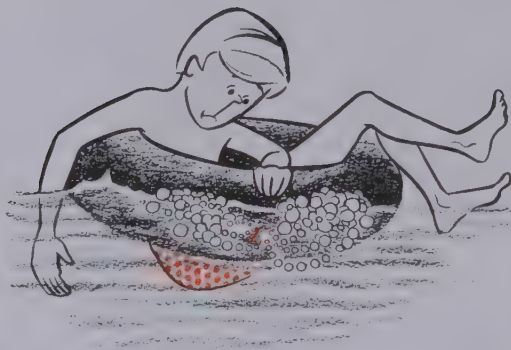
Self-Test *(Answers on pp. 319, 320)*

- Calculate the molecular or formula weights of the following formulas:
 - $(\text{NH}_4)_3\text{PO}_4$
 - MgSO_4
 - K_2CO_3
 - $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_3$
 - N_2O_5
- Write formulas for the following substances:
 - iodine
 - zinc chloride
 - copper(II) sulfide
 - ammonium acetate
 - barium phosphate
- Name the following compounds:
 - FeCl_2
 - $\text{Al}_2(\text{SO}_4)_3$
 - N_2O_3
 - MnO_2
 - Cr_2O_3
- Balance the following chemical sentences and state the types of reaction represented:
 - $\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$
 - $\text{K} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2$
 - $\text{PbO}_2 \rightarrow \text{PbO} + \text{O}_2$
 - $\text{Cu} + \text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{Ag}$
 - $\text{Al}(\text{NO}_3)_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + \text{HNO}_3$

5. Given: $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$.
- If 196 g of Zn are used, how many moles of H_2 will be produced, assuming that the reaction is complete?
 - How many grams of hydrogen are produced in step a?
6. What is the weight of 1 mole of the compound $\text{Fe}(\text{OH})_3$?
7. Given: $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
- If 3 moles of SO_2 are produced by the above reaction, how many grams of SO_2 are produced?
 - How many moles of oxygen molecules would be required for the reaction?
 - How many moles of sulfur would be required?
 - How many grams of sulfur would be required?
8. Given: $\text{Ca} + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$
- If 6.0 grams of hydrogen are produced by the above reaction, how many moles of hydrogen molecules are produced?
 - How many moles of calcium would be required to produce 6.0 grams of hydrogen?
 - How many grams of calcium would be required?
9. Given: $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$
- If 1.5 moles of oxygen molecules are produced in the above reaction, how many grams of oxygen are produced?
 - How many moles of KClO_3 would be required for the reaction?
 - How many grams of KClO_3 would be required?
10. (Assertion-Reason; see special directions in Appendix 13)
- | ASSERTION | REASON |
|-----------------------------|---|
| KCl is an empirical formula | Because the compound is composed of ion pairs instead of molecules. |

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- Chapter 5 of this handbook contains material on formulas, equations, and the mole concept, with accompanying problems and exercises.
- Johnsen, Russell H. and Ernest Grunwald, *Atoms, Molecules, and Chemical Change*, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.
- Chapter 6 contains a discussion on the atomic weight scale and molecular formulas, the determination of atomic weights, gram-molecular weights, and gram-molecular volume.
- Schaum, Daniel and Jerome L. Rosenberg, *Theory and Problems of College Chemistry*, McGraw-Hill Book Company, New York, 1966.
- A part of Schaum's Outline Series. Contains good discussions on atomic weights, molecular weights, and moles, along with many sample problems and practice problems.





PROPERTIES OF THE GASEOUS STATE

OBJECTIVES:

By the time you have completed your study of Chapter 9, you will be expected to demonstrate acceptable performance on the following objectives.

1. State the assumptions in the kinetic molecular theory of matter.
2. Apply the kinetic molecular theory to explain the following observed properties of gases: (a) indefinite volume, (b) compressibility, (c) rapid diffusion.
3. Apply the principles of intermolecular bonding to explain:
 - a. Why the condensation temperature of H_2 is -253°C at 1 atmosphere, while that of CCl_4 is 77° , even though both compounds have nonpolar covalent molecules.
 - b. Why H_2O has a condensation temperature of 100°C at 1 atmosphere and NaCl has a condensation temperature of 1413°C under the same pressure.
4. State the standards for measuring the temperature and pressure of gases.
5. Apply the kinetic molecular theory to explain why the volume of a gas varies inversely as the pressure, provided the temperature is constant.
6. State three ways in which real gases are different from the ideal gas model.
7. Apply the principles of intermolecular bonding to explain why gases do not conform to Boyle's Law at high pressure and why they do not conform to Charles' Law at very low temperatures.
8. Apply the laws of molecular composition to calculate at S.T.P.:
 - a. The molecular weight of a gas, given the density.
 - b. The density of a gas, given the formula.
9. Calculate the partial pressure of a gas collected over water in the laboratory, given the experimental data.
10. Calculate the number of moles of gaseous reactants and products involved in a chemical reaction, given the balanced equation.
11. Apply the general gas law to solve problems dealing with changes in temperature, pressure, and volume, given the experimental data.
12. Apply the principles affecting gaseous solutions to explain why carbonated beverages should not be stored in a warm place.

SUGGESTED ORDER OF STUDY

1. Perform Exp. 9-1. ✓
2. Study Secs. 9-1 through 9-4.
3. Perform Exp. 9-2. ✓
4. Perform Exp. 9-3. ✓
5. Study Secs. 9-5 through 9-10.
6. Perform Exp. 9-4. ✓
7. Study Secs. 9-11 and 9-12.
8. Perform Exp. 9-5. ✓
9. Perform Exp. 9-6. ✓
10. Do the Practice Exercises.
11. Review and do supplementary reading.
12. Take the Self-Test; review as needed.
13. Take test on Chapter 9.

9-1 • PROPERTIES OF GASES

Up to this point we have most often examined the chemical interactions of solutions made by dissolving solids in liquids. It is time to direct some attention to the third state of matter, gases. Our study of gases will deal with their physical properties more than with the chemical properties.

Historically, the study of gases has been important because it provided a key to an understanding of both physical and chemical changes. The information obtained by observing the behavior of gases has led to the development of the kinetic molecular theory of matter, to a more thorough understanding of temperature, and to new insight about the nature of forces which molecules exert upon each other. It may surprise you to know that chemists understand gases better than they do liquids or solids.



Gases have four characteristic properties that distinguish them from liquids and solids.

1. *Gases have no definite shape or volume.* The shape and volume of a gas is determined by the size and shape of its container. It completely fills any container. Why should a gas have no definite shape? Solids have a definite shape. Why should a gas completely fill a container? Liquids do not. What theory can we propose to account for this characteristic property of gases?
2. *Gases are compressible.* If you have ever inflated a tire or a balloon, you have demonstrated the compressibility of gases. The tire and the balloon become larger because of increased pressure on the inside; the gas inside is compressed.
3. *Gases diffuse rapidly.* If you remove the stopper from a bottle of perfume, you can soon smell the sweet-smelling vapor (gas) in all parts of the room.
4. *Gases have low density.* The solid state of a substance is about 1000 times as dense as its gaseous state. For example, oxygen gas has a density of 1.43 grams per liter at 0°C and normal pressure, whereas solid oxygen at -252.5°C has a density of 1,430 grams per liter.

9-2· THE KINETIC MOLECULAR THEORY

How can we explain the properties of gases? Scientists have proposed a theory to explain the observed properties of gases and have constructed a mental model to describe the behavior of an *ideal* gas which can help us greatly in understanding these properties. The theoretical description applies to an imaginary, or an ideal, gas. Just as there is no one person who is an “ideal student” or an “ideal citizen,” so there is no one real gas that fits the model exactly. The model is called the *kinetic molecular theory*, and the major assumptions in it are summarized as follows:

1. A gas is composed of very tiny molecules, widely separated. The molecules are so small in comparison to the average distance between molecules that we can think of them as occupying practically no volume in their container.
2. The molecules are in rapid, straight-line motion.
3. The molecules collide frequently with each other and with the walls of the container, but the collisions are perfectly elastic. That is, there is no net loss of energy as a result of the collision.
4. The number of molecules per unit volume of a gas at constant temperature and pressure is always the same.
5. At any given temperature, the molecules in a gas have the same average kinetic energy, but individual molecules may possess differing amounts of energy.

Let's now use the kinetic molecular theory to explain the stated properties of gases. Both the indefinite volume and the diffusion of gases can be explained by the fact that gaseous molecules are so small and so far apart that they behave essentially like independent particles. They move through space until they strike another molecule or the walls of the container.

This accounts for gas pressure also. The pressure exerted by a gas is a result of the total force of the collisions of the molecules on the walls of the container. The constant bombardment of the container by the molecules can be measured, and if we increase the number of molecules in the container, the pressure increases. The pressure drops when molecules are removed from the container.

The vast amount of space between gas molecules accounts for their low density. They are much farther apart than the molecules in a liquid or a solid.

At any given temperature the gas molecules in a sample have the same average kinetic energy. Some will have more kinetic energy than others, but most have a kinetic energy value close to the average. We use this average kinetic energy of a gas sample to represent the energy of all the particles in the sample. Increasing the temperature increases the average kinetic energy, because it increases the rate at which the molecules move.

9-3· INTERMOLECULAR FORCES IN GASES

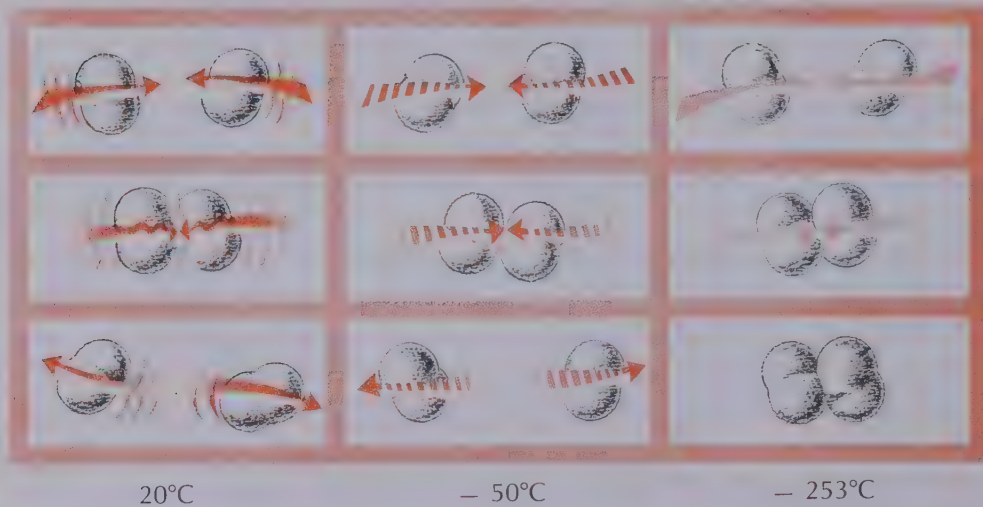
As we remove heat from a gas, we can lower the temperature sufficiently for it to become a liquid. The lowest temperature at which a substance remains gaseous at normal atmospheric pressure is known as its *condensation temperature*. As heat is removed at the condensation temperature, many of the mole-

cules no longer possess sufficient energy to overcome the attractive forces between them, and they pack closer together. The substance is then a liquid. An examination of the condensation temperatures of substances provides a clue to the magnitude of the force of attraction between their molecules. (See Table 9-1.)

Condensation Temperatures as Related to Type of Molecule			
Name of Substance	Formula of Substance	Type of Molecule	Condensation Temperature (1 atm., °C)
Hydrogen	H_2	Nonpolar (Lower molecular weight)	-253
Oxygen	O_2		-183
Methane	CH_4		-162
Ammonia	NH_3	Slightly polar	-33
Carbon Tetrachloride	CCl_4	Nonpolar (Higher molecular weight)	77
Benzene	C_6H_6		80
Water	H_2O	Strongly polar	100
Sodium Chloride	$NaCl$	Ionic (nonmolecular)	1413
Iron	Fe	Metallic (nonmolecular)	3000

Table 9-1

Suppose, for example, two gaseous hydrogen molecules approach each other, both moving at high speed. If these two molecules collide, they will then bounce off in new directions.



Under what circumstances will hydrogen liquefy?

On the other hand, if they were not moving as rapidly and if they were at a lower temperature, we might expect that they would be more influenced by the small attraction that hydrogen molecules have for each other. However, at this lower temperature, say about $-50^{\circ}C$, they would still be moving fast enough on the average to bounce off, as before. Only if the temperature is very, very low, $-253^{\circ}C$ or lower at a pressure of one atmosphere, are some hydrogen molecules moving slow enough not to

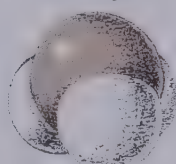
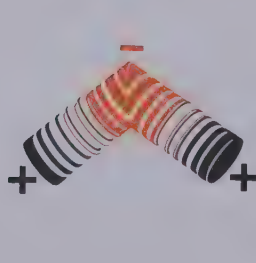
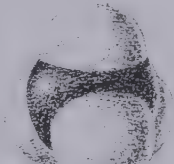
glance away after a close collision. At least, not glance away very often. At a temperature of -253°C or lower, the total energy of most of the hydrogen molecules in a sample is not enough to overcome the attractive forces between molecules.

Notice in Table 9-1 that the condensation temperature for oxygen is -183°C . At this temperature, and at lower temperatures, the total energy of oxygen molecules is not enough to overcome the attractive forces. Evidently, the attractive forces for oxygen molecules are stronger than the attractive forces for hydrogen molecules. For oxygen molecules the attractive forces can overcome energies at a temperature of -183°C or lower. The attractive forces for hydrogen molecules are so small that they cannot overcome the total energy of the hydrogen molecules until they are slowed down to the speed represented by -253°C . Table 9-1 provides clues to the relative strengths of molecule-to-molecule attractive forces. These forces are weakest for hydrogen and strongest for iron (of the substances listed).

When you stop to think about it, it is interesting to realize that you can measure attractive forces with a thermometer, by measuring the condensation temperature of a gas. The attractive force between a person and the earth is measured with a bathroom scale, usually. How could you measure the attractive force between two persons who are friends?

In general, nonpolar molecules of low molecular weight, such as oxygen or hydrogen or methane, CH_4 , have weak attractive forces. These weak forces are called van der Waals forces; they were discussed in Chapter 7 as part of the consideration of bonding, and they will be discussed further in Sec. 9-8. This is one way to identify nonpolar molecules. Polar molecules have stronger attractive forces. Ionic compounds and most metals have still stronger attractive forces.

Hydrogen bond forces tend to hold such molecules as NH_3 and H_2O together. These are polar covalent substances of low molecular weight, but their condensation temperatures are much higher than other low molecular weight molecules in which hydrogen bonding does not occur. Which has the stronger hydrogen bond forces, water or ammonia?

 NH_3  H_2O  CH_4 

The polarity of NH_3 , H_2O , and CH_4 .

Ionic compounds and metals exist in the gaseous state only at temperatures far above room temperature. This indicates that the forces in ionic and metallic bonds are quite strong, as we have observed in previous chapters. So, once again our knowledge of atomic structure and bond types is a key to understanding the behavior of matter.

9-4. STANDARD TEMPERATURE AND PRESSURE

We have indicated that gases are very sensitive to changes in temperature and pressure. In fact, it is meaningless to state the volume of any gas unless we specify the temperature and pressure at which this volume is measured. Therefore, it is imperative that we have some standard for measuring gas volumes. Scientists have agreed that the *standard temperature should be 0° Celsius*. This standard is the temperature of melting ice and was chosen because it is convenient and easily produced in the laboratory.

Standard pressure is the pressure exerted by a column of mercury exactly 760 mm high. We define pressure as the force per unit area that molecules exert on the walls of their container. Atmospheric pressure can be measured with a barometer. The mercury barometer was first constructed by Torricelli about 1650. It consists of a glass tube about 3 feet long which is sealed at one end. The tube is filled with mercury and inverted. The open end is placed in a cup of mercury. Some of the mercury in the tube flows out into the cup, leaving an empty space above the mercury which contains a small amount of mercury vapor, but is nearly a perfect vacuum. The height of the mercury column is determined by the force per unit area which the atmosphere exerts on the mercury in the cup. At sea level under normal conditions, the height of the column is 760 mm, and we say that the pressure is 760 torr, or one atmosphere (atm.).

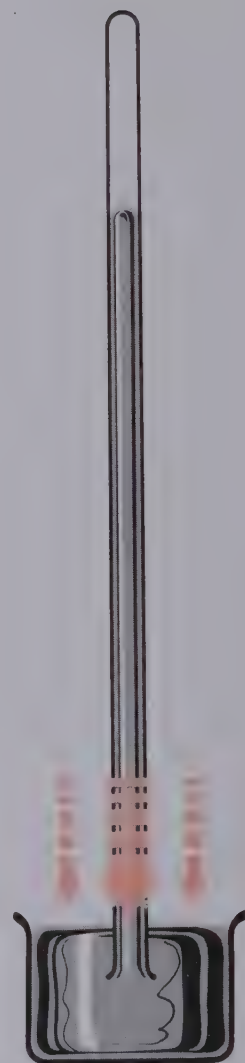
When performing experiments involving gases, you must always record the barometric pressure in your classroom. Learn how to read the barometer with precision, because a slight error in recording this value may result in a large error in your calculations.

It is common practice to abbreviate standard temperature and pressure as S. T. P.

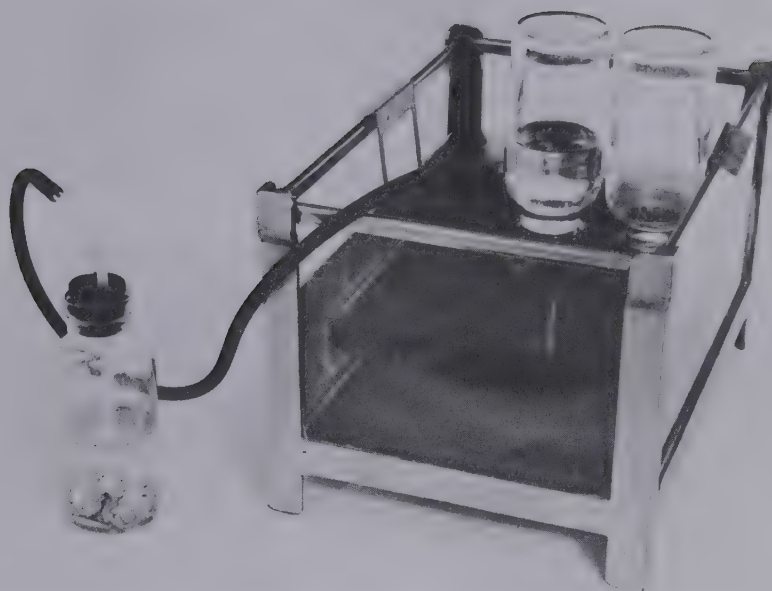
9-5. COLLECTING GASES IN THE LABORATORY

Gases may be collected over liquids such as mercury, but in elementary work we usually collect them over water. This is because water is available and because mercury vapors are dangerous. When a gas is collected over water, certain factors must be considered in making calculations.

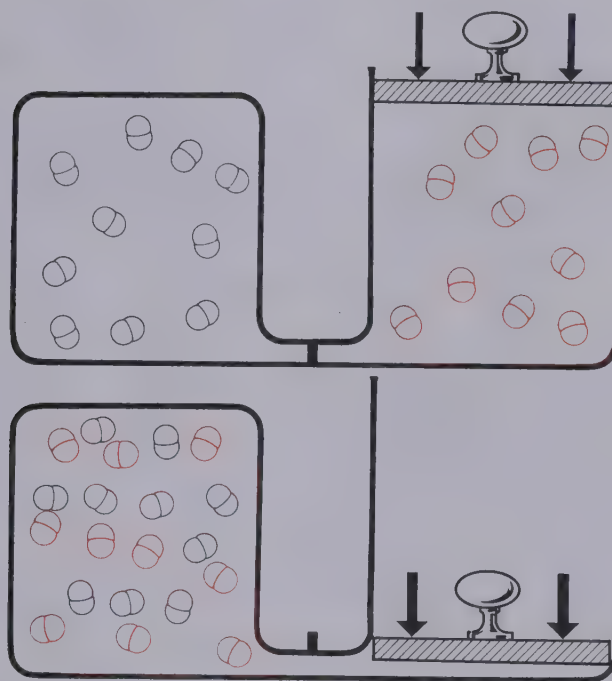
First, we will be interested in determining the exact pressure of the dry gas in our collecting tube. We must remember that a part of the gas in the tube is the gas we have produced and a part of it is water vapor that got there because we bubbled the gas through the water. To determine the pressure exerted only by the dry gas, we apply *Dalton's Law of Partial Pressures*. This law states that *the total pressure of a mixture of gases is the sum of the partial pressures of each gas*. Each partial pressure is the part of the pressure each gas would exert if it were the only one present. For example, suppose that the



A mercury barometer.



An apparatus for collecting a gas by water displacement.



In separate chambers the two kinds of molecules exert pressure independently of each other. When placed together in the same chamber, they exert the sum of the individual pressures.

total pressure of the gas we have produced, plus the pressure of the water vapor, was 745 torr. Suppose that we knew, somehow, that the pressure of the water vapor was 19 torr. Then, by subtracting 19 torr from 745 torr, we calculate that the pressure of the dry gas is 726 torr (745 torr – 19 torr). This leaves us with two questions: "How do you know the pressure of the water

vapor?" and "How do you know the total pressure of the gas plus the water vapor?" The answer to both questions is, "From laboratory measurements."

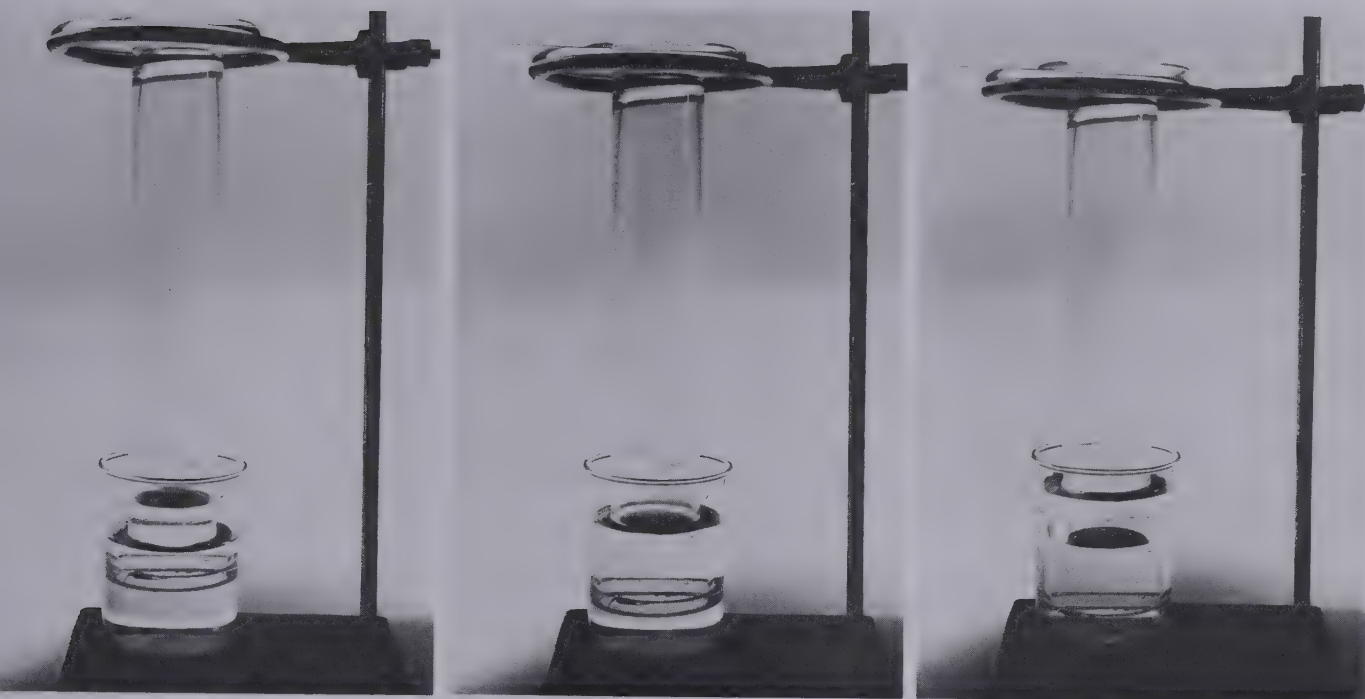
From laboratory measurements of water vapor only, the vapor pressure of the gaseous water in dynamic equilibrium with liquid water has been determined. A table of the vapor pressure of water at various temperatures is given in Appendix 8. For example, when liquid water is at a temperature of 21°C , its vapor pressure is 19 torr.

Why does a carbonated beverage rise in a straw when you suck on the end of the straw? Below is a picture showing some of the liquid partially drawn up in one straw. The pressure of the atmosphere outside of the straw is greater than the pressure of the air inside the straw, because sucking on the straw reduces the pressure of the air inside it.



The level of the liquid inside the other straw is below the level of the liquid outside the straw. You can tell from this that the person on the top end of the straw has blown into it a little bit, increasing the pressure inside the straw and making it greater than the pressure of the atmosphere outside the straw.

When the pressure inside the straw is the same as that outside it, the level of the liquid inside the straw is the same as the liquid level outside the straw. The illustration below shows three tubes, each containing a gas and some water vapor. In which tube is the total pressure of the gas plus the water vapor higher than the pressure of the atmosphere outside the tube? In which tube is the pressure inside less than the pressure outside? And in which are the pressures equal?



In which photo is the inside gas pressure equal to the gas pressure outside the cylinder?

In the laboratory if the pressure inside the tube is not equal to the pressure outside, you can make the pressures equal by raising or lowering the container. One way or the other, by raising or lowering, the level of the liquid inside can be adjusted until it is the same as the level of the liquid outside. Then the pressure inside is the same as the pressure outside. The pressure outside can be measured with the barometer.

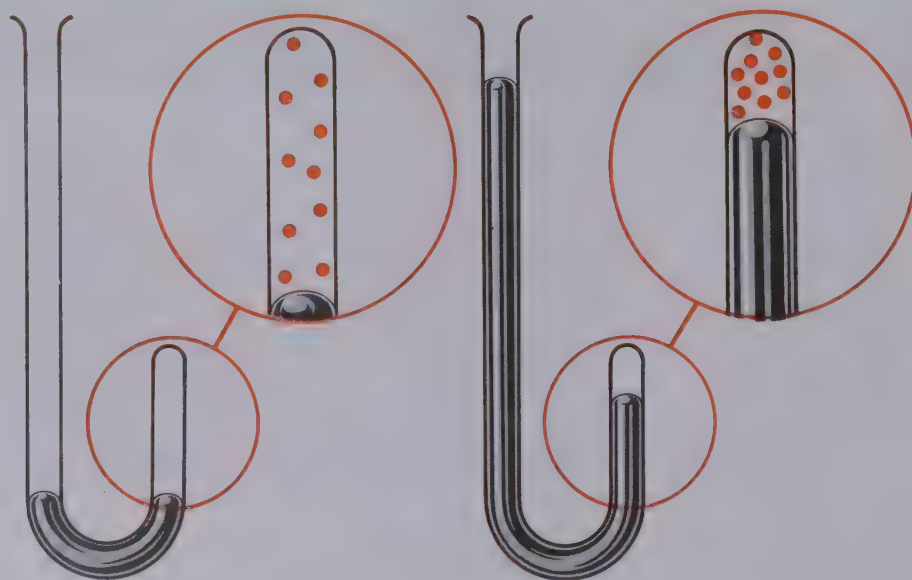
To summarize: When you are collecting a gas over water and it is necessary to know the pressure of the gas:

1. Do not completely fill the collecting vessel with the gas; leave a little water at the bottom.
2. Raise or lower the collecting vessel enough so that the level of the water inside is the same as the level of the water outside.
3. Determine the temperature of the water and look up the vapor pressure of water for that temperature in the table in Appendix 8.
4. Read the barometric pressure of the air in the laboratory.
5. The difference between the barometric pressure and the vapor pressure of water that you have obtained from the table is the pressure of the gas that you have collected.

9-6 • THE EFFECT OF PRESSURE ON THE VOLUME OF A GAS

Scientists had long been aware of the fact that air could be compressed, but prior to the seventeenth century no one had made a careful study of it. Robert Boyle (1627–1691), an English physicist, carried out extensive experiments dealing with the effect of pressure on gas volumes. He published his results in 1662.

Boyle used a glass tube bent into the shape of a J. The top of the short arm was sealed, and the top of the long tube was open. A small quantity of mercury was placed in the tube and the level adjusted so that the height of the mercury in each arm was equal. This traps a quantity of air above the mercury in the short arm. At this point, the pressure of the trapped air is equal to atmospheric pressure. By measuring the heights of the two mercury columns as successively greater quantities of mercury were added to the open arm, the relationship between the pressure and volume of air could be determined. When the pressure is increased by one-third, the volume of the air decreases by one-third. If the pressure on the air is doubled, the volume drops to one-half the original volume. These observations are summarized into a statement known as *Boyle's Law: the volume of a given mass of gas varies inversely as its pressure, provided the temperature remains constant.*



Why do the same particles exert greater pressure in less space?

How can this be explained? On the basis of the kinetic theory we assume that gases are composed of rapidly moving molecules which bombard the walls of their container and that the space occupied by the molecules is negligible. If we place a given sample of gas in a container, the molecules spread

out uniformly, and the effect of bombarding the container walls produces a pressure which we will call P . If we reduce the size of the container by one-half, what happens to the pressure? Since there are still the same number of molecules present, but only one-half the original space is available to them, they strike the walls of the container twice as often. This results in doubling the pressure, P , and now it becomes $2P$.

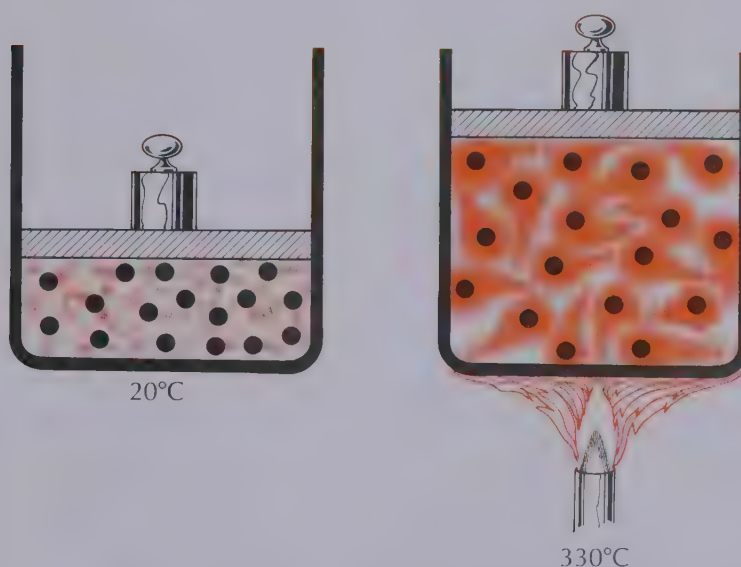
If the container is increased to twice its original size, the molecules have twice as much space in which to move, so they strike the walls one-half as often (on the average). Therefore, we would expect the pressure to become $\frac{1}{2}P$.

We have said that Boyle's Law holds true for gases *if* the temperature does not change. What effect does changing the temperature have on the volume of the gas?

9-7. THE EFFECT OF TEMPERATURE ON THE VOLUME OF A GAS

In 1790, Jacques Charles, a French scientist, carried out a laboratory study of the relationship between temperature and gas volume. He found that if a gas sample is heated or cooled while the pressure is kept constant, the volume of the gas increases or decreases in direct proportion to the rise or fall in temperature. He found that the fractional increase or decrease in volume per degree rise or fall in temperature is essentially the same for all gases, even though their chemical composition is different.

Under normal conditions, and at temperatures near 0°C , the volume of all gases changes by roughly $1/273$, or 0.37% , for each Celsius degree that the



How can the same particles exert the same pressure in a larger space?

temperature is changed. Charles assumed that this same relationship would continue if temperatures were raised or lowered beyond the range of his experiments. By plotting a graph of experimental data, and by extrapolating the line obtained, he found that it crosses the temperature axis at -273°C . This means that at a temperature of -273°C a gas would be expected to have zero volume! However, all gases become liquids before reaching that low a temperature, and the volume-temperature relationship for gases does not apply to liquids.

Examine the temperature scales depicted in the drawing. If the point at -273°C is considered the origin, or the absolute zero point, then we can convert all Celsius readings to a new scale by adding 273 to each reading. This is exactly what is done in constructing the Kelvin temperature scale. (It used to be called the absolute scale.) Temperatures measured on this scale are called *absolute temperatures* and are given in degrees Kelvin (abbreviated $^{\circ}\text{K}$). *The volume of a gas is proportional to its absolute temperature, provided the pressure remains constant.* This is commonly known as *Charles' Law*. To state the law in another way: if the pressure does not change, the volume of a gas increases about $1/273$ of its volume at 0°C for each degree rise in temperature. Conversely, the volume decreases about $1/273$ of its value at 0°C for each degree the temperature is lowered, provided the pressure is constant.

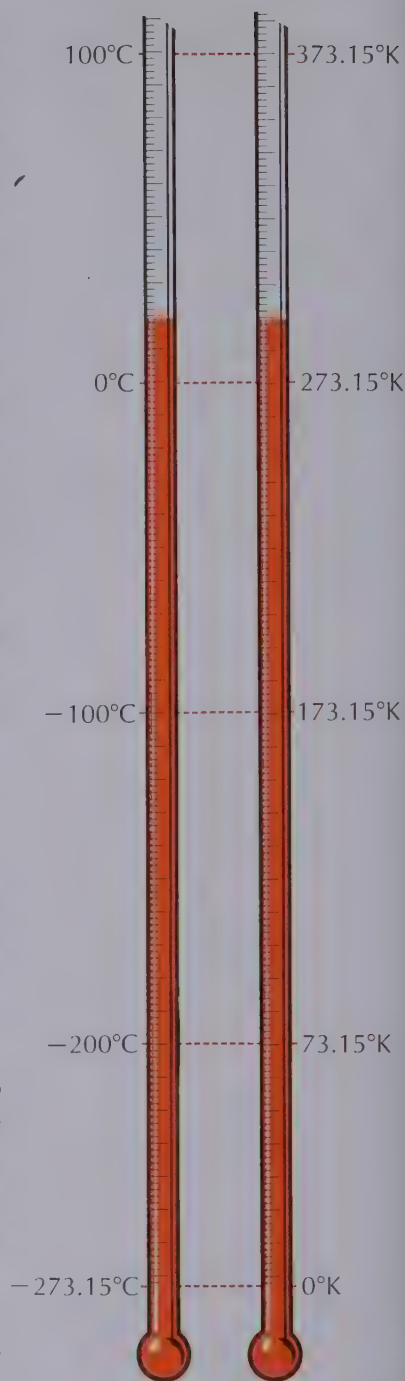
9-8. REAL GASES COMPARED TO AN IDEAL GAS

Boyle's Law and Charles' Law describe the behavior of an ideal gas. According to the assumptions in the kinetic molecular theory, molecules of an ideal gas are considered to be tiny particles which occupy no volume. These molecules are able to collide with no loss of energy because there are no attractive forces, and a sample of an ideal gas would continue to contract if the pressure is increased or the temperature is decreased until it reached zero volume.

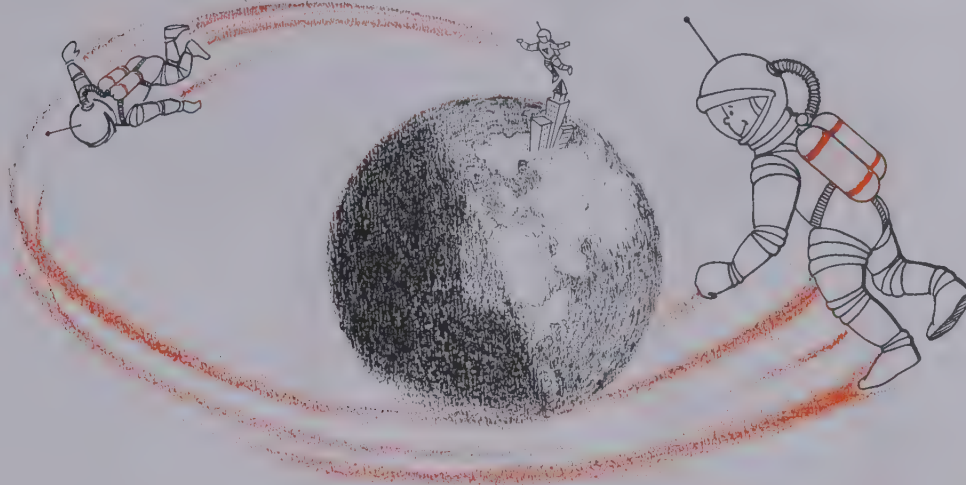
Real gases do not conform to this model because their molecules do occupy volume; they do have some attraction for each other; and they liquefy before reaching a temperature of absolute zero. But within the normal ranges of temperature and pressure, most real gases conform closely to the behavior of an ideal gas; carbon dioxide is one commonly known gas which deviates from the behavior of an ideal gas as it has rather strong attractive forces.

These attractive forces are the van der Waals forces you learned about in Chapter 7. When the Dutch physicist, Johannes van der Waals, studied the behavior of real gases about 100 years ago, he noticed that they deviated from the behavior that would be expected if the gas molecules had zero volume and did not attract each other. He deduced that real gas molecules must have a small volume and that they attract each other to some extent. We have already learned about these attractive forces in our examination of Table 9-1 and in thinking about attractions among sugar molecules in Chapter 7. Let us once again think about the possible cause of the van der Waals attractive forces, this time for gas molecules instead of sugar molecules.

Imagine that two oxygen molecules approach each other. When this happens, their electrons repel each other, and their nuclear charges also repel each other. But there is an attraction of each electron of one molecule for the



nuclei of the other molecule. These attractive and repulsive forces are in balance at a distance of a few angstroms (one angstrom, \AA , equals 10^{-8} cm). At internuclear distances from about 4 to 10\AA , there is a net attractive force. Such forces are quite weak and vary inversely to the sixth power of the distance between particles. (If the force of attraction between you and the earth varied inversely to the sixth power of the distance, you could climb on the top of a



high building, jump upward vigorously, and sail off into space. But on the earth's surface you would weigh more than you do now. It is perhaps a good thing that the force of gravitation varies inversely only to the second power of the distance of separation.) That is, forces of attraction which vary inversely to the sixth power of the distance of separation are very weak unless the particles are very close, and then they are much, much stronger. These van der Waals forces are more effective when molecules or ions, or other small particles, are very close together. They influence the properties of gases and are also important in determining the properties of solids and liquids if other, stronger forces are not important. Thus, gasoline molecules are held close together, as a liquid substance, by these forces. Candle wax is a solid for this reason. The sticking property of glue is due in large part to van der Waals forces. To some extent it is these forces that hold the molecules of your body in place.

Boyle's Law does not apply very well to real gases at high pressures, because under these conditions the molecules are close enough that the van der Waals forces come into play, and the molecules attract each other. At high pressures a gas begins to assume the properties of the liquid state.

Charles' Law does not hold very well for real gases at extremely low temperatures. As the temperature is lowered, the energy of the molecules decreases to the point where van der Waals forces become more effective, and as molecular attraction increases, the gas is nearing the point of becoming a liquid.

9-9. THE EFFECT OF PRESSURE ON THE SOLUBILITY OF GASES

Pressure does not affect the solubility of solids and liquids to any appreciable extent, but it is important in determining the solubility of gases. Carbonated



Explain what happens to the molecules of carbon dioxide when you open a can of carbonated beverage.

beverages effervesce, or fizz, when poured from the container into another container. These beverages are made by forcing carbon dioxide gas into a flavored solution under a pressure of about 10 atmospheres. While under pressure, the gas-liquid solution is sealed in bottles or cans. When the cap is removed, the pressure on the liquid is reduced to atmospheric pressure (one atmosphere), and some of the carbon dioxide gas escapes rapidly from the solution.

This is in accordance with Le Chatelier's Principle. The capped container of beverage contains an equilibrium solution in which the rate of gas entering solution equals the rate at which the gas is escaping into the space above the liquid in the container. But when the pressure is suddenly reduced, the system reacts in such a way as to try to restore equilibrium. The result is an increase in the rate at which gas comes out of solution.

9-10. THE EFFECT OF TEMPERATURE ON THE SOLUBILITY OF GASES

Many gases are more soluble in cold water than in warm water. A glass of cool water drawn from the tap in the laboratory and allowed to stand in a warm room for a time will develop small bubbles along the inner surface of the glass. These bubbles contain air which was dissolved but is now escaping from the water as it warms.



Why do you keep a carbonated beverage in the refrigerator instead of on the stove?

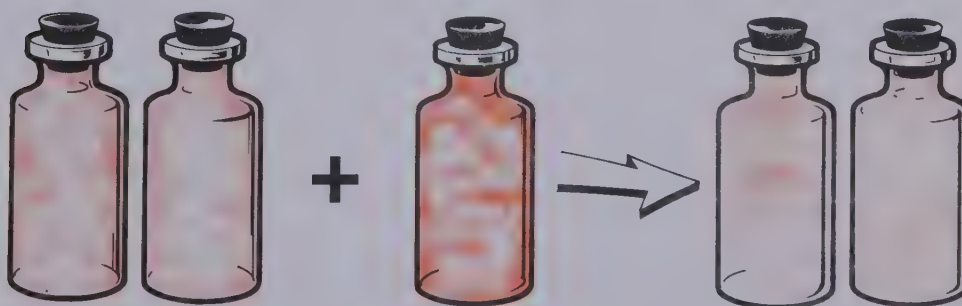
Raising the temperature of a solution increases the average speed of its molecules and causes the dissolved gaseous molecules to leave the solvent at a more rapid rate than undissolved gaseous molecules enter the solvent. Gas molecules in a solution are less random than those not in solution. Therefore, the tendency toward maximum randomness is favored by the gaseous state.

9-11 • THE MOLECULAR COMPOSITION OF GASES

Gases are very similar to each other in their physical behavior. They also combine in chemical reactions in simple volume ratios. In Chapter 5 we mentioned the work of Gay-Lussac and Avogadro in the development of atomic theory. Let us review their findings at this time.

Gay-Lussac's Law of Combining Volumes

About the time Dalton was developing his atomic theory, Gay-Lussac studied a number of reactions in which gaseous elements combined to form gaseous compounds. He found the following relationships to exist:



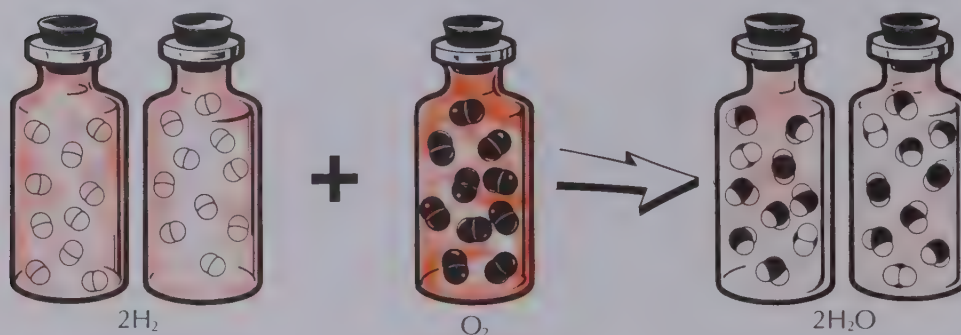
(1) hydrogen + oxygen \rightarrow water vapor
 2 vols. 1 vol. 2 vols.

- (2) hydrogen + chlorine \rightarrow hydrogen chloride
 1 vol. 1 vol. 2 vols.
- (3) nitrogen + hydrogen \rightarrow ammonia
 1 vol. 3 vols. 2 vols.

Gay-Lussac summarized his observations by saying that when gases combine to form a gaseous product, the volumes are in the ratio of small whole numbers. This law of combining volumes tells us *how* gases combine, but does not explain *why*. Avogadro's Theory attempts to explain why.

Avogadro's Theory

The apparent conflict between the law of combining volumes and Dalton's atomic theory was resolved in 1811 when Avogadro proposed that the physical particles of the gaseous elements were not necessarily single atoms, but could be molecules composed of two or more atoms. He reasoned that equal



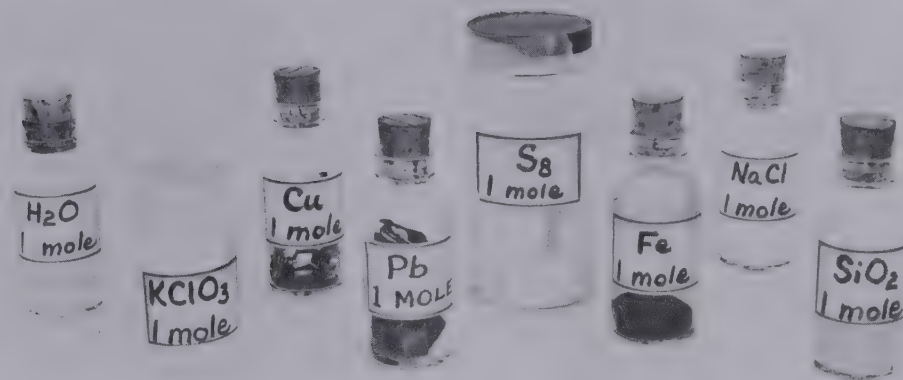
volumes of different gases, measured at the same temperature and pressure, probably contained equal numbers of particles. In one kind of gas, these particles might be single atoms. In a different gas, the particles might be molecules with two atoms in each molecule. In still another gas, with the same total number of particles, the particles might be composed of three atoms each, and so on. If this is correct—if molecules of hydrogen and of oxygen are each composed of two atoms of hydrogen and two atoms of oxygen—then the molecules could break up into atoms during a chemical reaction. The atoms then might rejoin to form water, which could have molecules with three atoms in each, two atoms of hydrogen and one atom of oxygen.

Molar Volume

Avogadro's Theory can be interpreted to mean that one liter of hydrogen, oxygen, chlorine, water vapor, ammonia, or of any other gas, each contain the same number of molecules when they are all at the same temperature and pressure. Of course, some other volume of gas, such as two liters, fits the same theory: The same number of molecules are in two liters of oxygen at S.T.P. as the number of molecules in two liters of hydrogen at standard temperature and pressure.

One of the outcomes of the work of Robert Millikan, mentioned in Chapter 5, was the determination of the actual number of molecules of a gas with a

volume of 22.4 liters at S.T.P. This number turned out to be 6.02×10^{23} ; it is called *Avogadro's Number* and is the number of particles in a mole.



Contrast the space occupied by a mole of gas with that occupied by the mole amounts of the water and solids.

The reason why 22.4 liters was selected turns out to be an interesting story. You remember from Chapter 5 that Dalton's atomic theory proposed a model in which each atom of any element had a certain weight, and all atoms of that element had the same weight. The question was, what is the weight of an atom of any element, such as oxygen, or hydrogen, and so on? No one in those days, about 200 years ago, could figure this out, so Dalton proposed the idea of relative weights, as you know from your study of Chapter 5. For example, Dalton suggested that everyone agree that the relative weight of a hydrogen atom be selected as 1.0.

Since there are two atoms of hydrogen in a molecule of hydrogen, according to Avogadro's ideas, the relative weight of a hydrogen molecule would be 2.0. Now, it would be very helpful if there were some relation between relative weights and real weights. It turned out that at S.T.P., 2.0 grams of hydrogen molecules had a volume of 22.4 liters. *The special volume, 22.4 liters, is called a molar volume, from the word molecule.* The molar volume contains enough molecules (at S.T.P.) to weigh in grams the same as the relative weight of a molecule.

For example, if you wanted to know the relative weight of a molecule of oxygen, you could measure the real weight in grams of a molar volume of oxygen at S.T.P. It turns out to be 32.0 grams. So, we know the relative weight of a molecule of oxygen is 32.0. Today, it is common to speak of the molecular weight of oxygen as 32.0, instead of the relative weight as 32.0. At S.T.P., the weight of a molar volume of carbon dioxide is 44.0 grams; so, the molecular weight of carbon dioxide is 44.0.

At S.T.P., there are 6.02×10^{23} molecules of chlorine in 22.4 liters, or 6.02×10^{23} molecules of gas in 22.4 liters. So, we can say that 6.02×10^{23} molecules of oxygen weigh 32.0 grams, or a mole of oxygen molecules weighs 32.0 grams. A mole of carbon dioxide molecules weighs 44.0 grams. The molecular weight of oxygen is 32.0. The molecular weight of carbon dioxide is 44.0. The molecular weight, you can see, is a number; it is the number of grams

that a mole of molecules weighs; it is the number of grams that 22.4 liters of a gas weighs at S.T.P.

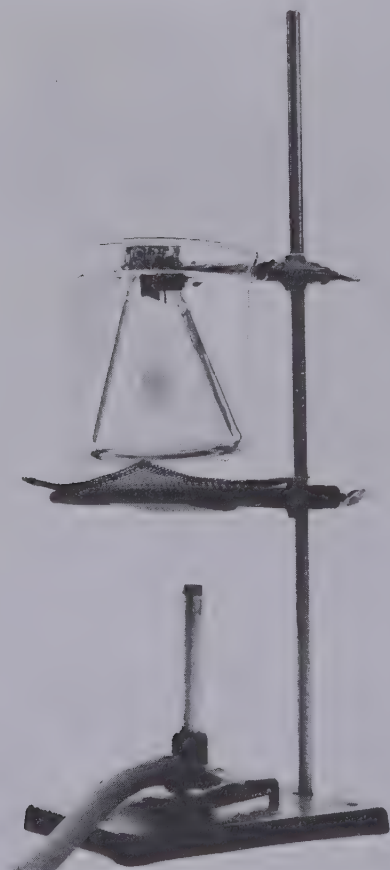
This information is summarized for some gases in Table 9-2.

At S.T.P. One Mole of Molecules of Any Gas Occupies 22.4 Liters			
Gas Name	Gas Formula	Weight of One Mole of Molecules (in grams)	Volume at S.T.P. (in liters)
Oxygen	O ₂	32.0	22.4
Hydrogen	H ₂	2.0	22.4
Carbon monoxide	CO	28.0	22.4
Carbon dioxide	CO ₂	44.0	22.4
Ammonia	NH ₃	17.0	22.4
Chlorine	Cl ₂	71.0	22.4
Nitrogen	N ₂	28.0	22.4

Table 9-2

9-12 · DETERMINING THE MOLECULAR WEIGHT OF A GAS EXPERIMENTALLY

From what you have learned, you can see that the molecular weight of a gas, a very important quantity, can be determined by obtaining 22.4 liters of the gas at S.T.P. and weighing it. However, it is inconvenient to do this, since 22.4 liters is a fairly large volume, about the size of a basketball, for example, and



How are all the items of knowledge about gases applied in the determination of molecular weights in Experiment 9-6?

it is not easy to handle this much gas in most laboratories. The problem of getting the gas at exactly zero degrees Celsius and 760 torr pressure adds to the difficulty.

But we can weigh a smaller, more suitable quantity of gas at a convenient temperature and pressure in the laboratory. Then we can apply the gas law relationships to calculate the weight of a molar volume of the gas at S.T.P. So, from the laboratory observations we have conveniently made, we can get the molecular weight. To do this, we measure the weight and volume of a gas sample in the laboratory and note the temperature and pressure. By applying the gas laws, we convert the measurements to the values they would have at S.T.P., and then the weight in grams of 22.4 liters of the gas can be calculated. The number of grams is the molecular weight of the gas.

9-13. QUANTITATIVE RELATIONSHIPS IN GASEOUS REACTIONS

To learn how to apply the information presented in this chapter to laboratory determinations with gases, refer to Appendices 8, 9, and 10 for sample calculations. Additional reading in resource material is also suggested. Working with gases in the laboratory requires care and precision, but is rewarding in that you can observe many of the properties that have been discussed in this chapter.

Suggestions for Creative Work

1. To illustrate Boyle's Law, devise an experiment which does not require the use of mercury and which is suitable for elementary chemistry students to perform without supervision.
2. To illustrate Charles' Law, devise a simple, effective, and safe demonstration which would make the effect of temperature on a gas volume understandable to students of junior high age.

Suggestion for Creative Writing

1. Write a short article, suitable for a family magazine, which points out certain safety precautions regarding the effects of temperature and pressure on gases. It should be interesting, attention-getting, and easily understood by the lay public.

Practice Exercises *(Answers on pp. 320, 321)*

Note: Sample problems which may help you in solving these problems are given in Appendices 8, 9, and 10. Also, many supplementary references provide numerous practice exercises.

1. If the volume of a gas at 700 torr is 250 cc, what pressure is required to reduce the volume to 200 cc, providing the temperature does not change?
2. A gas has a volume of 50 cc at S.T.P. What temperature is required to change the volume to 100 cc, providing the pressure does not change?
3. A gas measures 300 cc at 20°C and 750 torr pressure. Calculate its volume at 25°C and 770 torr.

4. A gas sample has a volume of 100 cc at 25°C and 740 torr. Calculate the volume at S.T.P.
5. Hydrogen is collected over water in the laboratory. The volume is 25 cc; the level of the water column inside the tube is the same as the level outside; the temperature is 25°C and the barometric pressure is 675 torr. The vapor pressure of water at 25°C is 24 torr. Calculate the volume of the dry hydrogen at S.T.P.
6. What is the weight of 1 liter of SO_2 gas at S.T.P.?
7. What is the density at S.T.P. of a gas whose molecular weight is 34.0?
8. If 250 cc of a gas weighs 0.179 g at S.T.P., what is its molecular weight?
9. Given: $\text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl}$.
 - a. How many moles of Cl_2 are required to produce 5 moles of HCl ?
 - b. How many molecules are in one mole of HCl ?
10. Given: $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$.
 - a. How many moles of O_2 can be produced by using 122.5 g of KClO_3 ?
 - b. What is the weight of this much O_2 ?
11. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION	REASON
Boyle's Law does not apply well at extremely high pressures	Because the molecular attraction at high pressure causes the gas to behave more like a liquid.

Self-Test *(Answers on pp. 321, 322)*

1. State the assumptions in the kinetic molecular theory of matter.
2. Apply the assumptions stated above to explain why gases are very compressible.
3. What is meant by S.T.P.?
4. Why does Boyle's Law not hold very well for gases at extremely high pressures?
5. A gas volume measures 200 cc. It is collected over water, and the level of the water column inside the tube is the same as that outside. The temperature is 23°C, and the barometric pressure is 675 torr. The vapor pressure of water at 23°C is 21 torr. What would be the volume of the dry gas at S.T.P.?
6. Given: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$.
 - a. How many liters of H_2 are needed to produce 150 liters of water vapor at S.T.P.?
 - b. How many moles of hydrogen is this?
 - c. How many moles of water vapor are contained in 150 liters at S.T.P.?
 - d. What is the weight of 150 liters of water vapor at S.T.P.?
7. A certain gas was collected in the laboratory. At S.T.P., it was found that 130 cc of the gas has a weight of 0.35 g. What is the density of the gas? What is its weight per mole?
8. A gas sample measures 100 cc at 0°C and 760 torr of pressure. At what new temperature and pressure would the sample still measure 100 cc?
9. A capped bottle of carbonated beverage was left in the sun, and after a time it exploded. Apply Le Chatelier's Principle to explain why this happened.

10. A certain gas has a density of 1.53 grams per liter at S.T.P. What is the molecular weight of the gas?
11. Calculate the density of hydrogen sulfide gas, H_2S , at S.T.P.
12. (Multiple Completion; see special directions in Appendix 13)
The following properties are characteristic of gases:
 1. They diffuse rapidly.
 2. They have low density.
 3. They have definite shape but indefinite volume.
 4. They are compressible.

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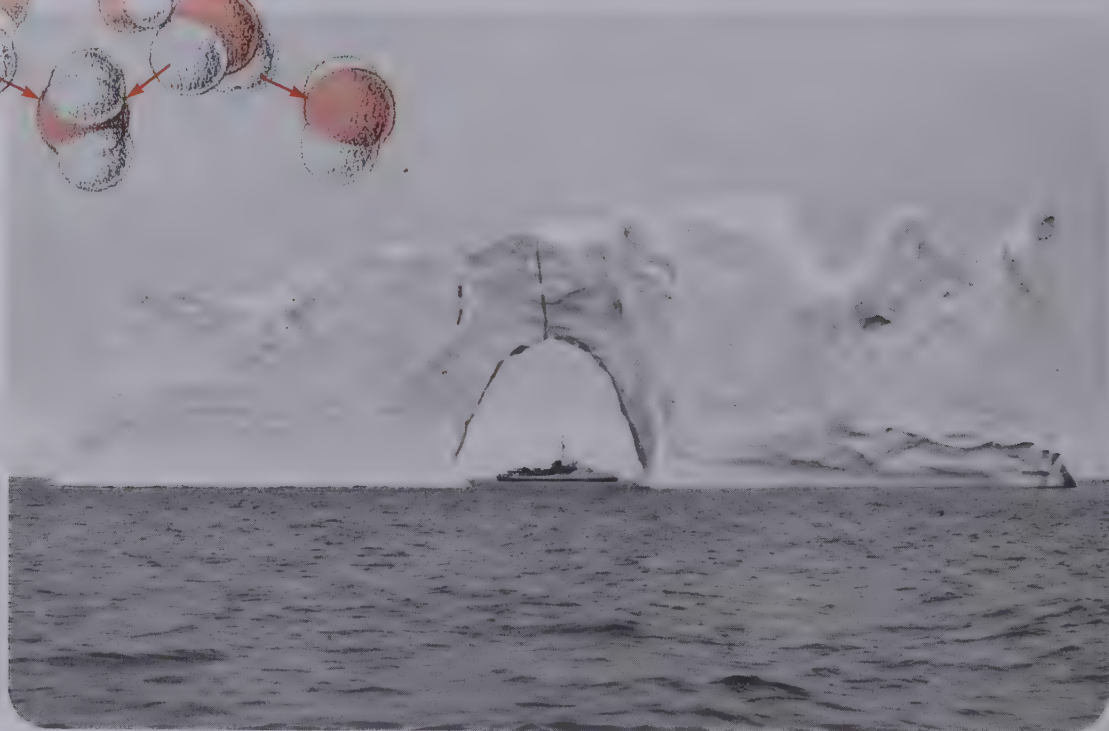
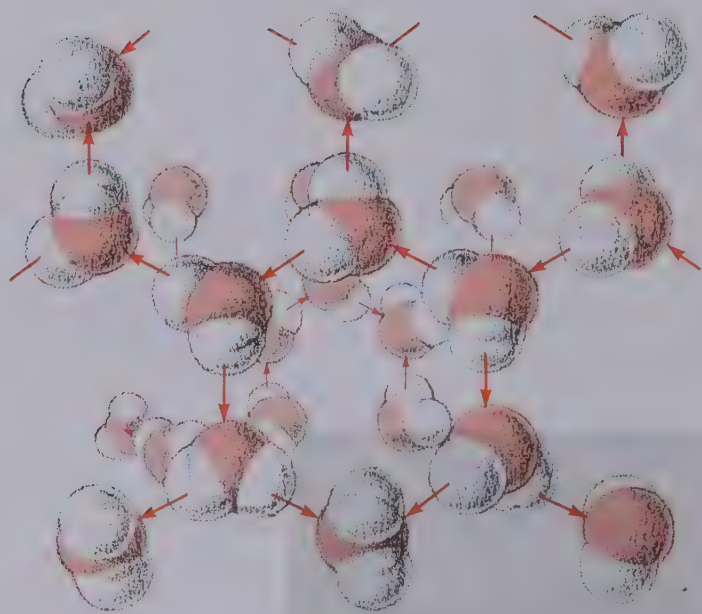
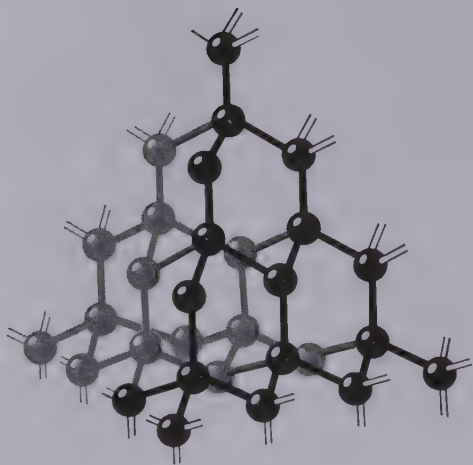
Chapter 10 discusses density, pressure, and Boyle's Law; Chapter 13 considers the temperature scales; Chapter 14 discusses heat and the kinetic theory of gases, real and ideal. Written for the non-technical student. Highly recommended.

Parsons, Cyril, and Clare Dover, *The Chemist at Work*, Ginn and Company, Boston, 1966.

Chapter 13 discusses the laws of partial pressure; Chapter 17 gives an excellent presentation on the solubility of gases. Many colorful and useful diagrams and illustrations. Highly recommended for all students.

Strong, Laurence E., "The Difference Is in the Kind of Energy," *The Science Teacher*, May 1968, 57.

Short commentary on misconceptions about the relationship between the energy of a liquid and its vapor. Makes an excellent point clarifying the kinetic-potential energy difference in a liquid and its vapor.



10

PROPERTIES OF SOLIDS AND THEIR SOLUTIONS

OBJECTIVES:

By the time you have completed your study of Chapter 10, you will be expected to demonstrate acceptable performance on the following objectives.

1. *State* the general properties of solids.
2. *Apply* the kinetic theory and the principles of bonding and intermolecular forces to explain why solids have their characteristic properties.
3. *Describe* the phenomena of deliquescence and efflorescence in solids and *suggest* how Le Chatelier's Principle applies.
4. *Apply* the tendencies toward minimum energy and maximum randomness to explain phase changes in solids.
5. *Predict* whether a solid is ionic, molecular, metallic, or a network solid, given the formula for the substance.
6. *Define* the term "unit cell" and *illustrate* three types of cubic unit cells.
7. *Recognize* the type of cubic crystal, given a model or a diagram of a cubic cell.
8. *Explain* why water has its maximum density at 4° C, using the effects of kinetic energy and hydrogen bonding.
9. *Cite* one practical application of the property of deliquescence.
10. *Cite* two methods for preparing crystals and *discuss* the advantages of each.
11. *Write* the ionic equation for the reaction that is expected to occur; given any two formulas for solutions used in Exp. 10-3.

SUGGESTED ORDER OF STUDY

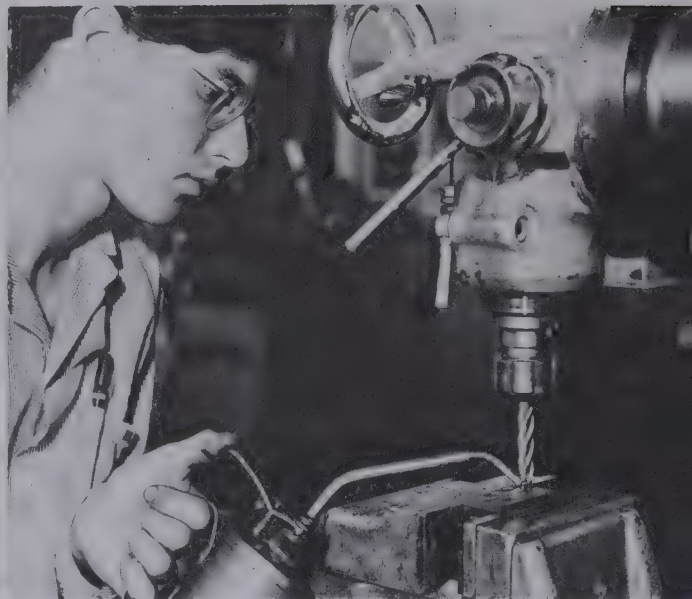
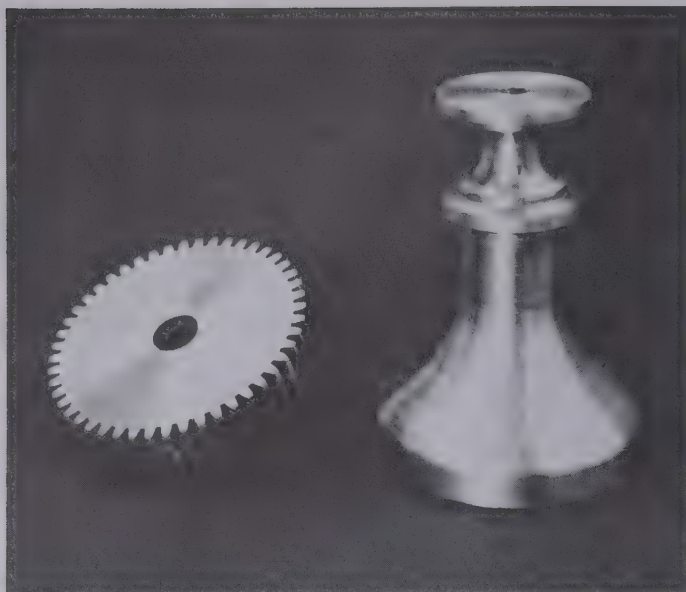
1. Perform Exp. 10-1. ✓
2. Study Secs. 10-1 through 10-7.
3. Perform Exp. 10-2. ✓
4. Study Secs. 10-8 through 10-10.
5. Perform Exp. 10-3. (Note: This experiment requires extensive preparation of data tables prior to the laboratory period.)
6. Do the Practice Exercises and review.
7. Take the Self-Test and review as needed.
8. Take the test on Chapter 10.

10-1 • PROPERTIES OF THE SOLID STATE

In Chapter 3 you studied the properties of liquids and solutions of solutes in water. In Chapter 9 you learned about the properties of gases. Now it is appropriate to look at the third state of matter, the solid state.

The general properties of solids are as follows:

1. *Solids have definite volume.* The forces of attraction (our model says) are sometimes strong, sometimes weak; but for all solids, they are at least strong enough to hold the particles together in relatively fixed positions and not permit the solid to change in volume.
2. *Solids have definite shape.* According to our model, this is because the particles making up the solid have fixed positions and are not free to move about.



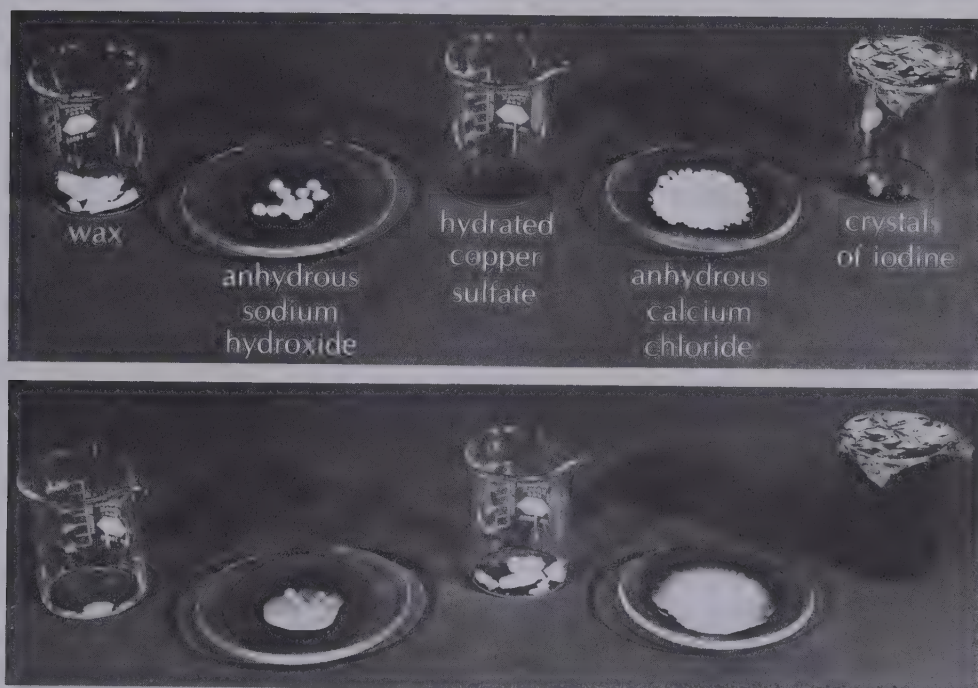
(Left) Solids, especially metals, can be shaped into many different forms. (Right) The student is using a milling machine to modify the shape of a piece of metal.

3. *Solids do not tend to diffuse.* Again, if the particles are fixed in position, they cannot diffuse.
4. *Many solids form crystals.* The particles that compose a solid, according to our model, remain near fixed positions. When the particles form a pattern, such solids are crystals. A few substances, such as glass or cold tar (in the winter time) have definite shape, definite volume, and do not diffuse. We certainly would say that glass is a solid, for example. But in glass and cold tar and in many solid plastics, the particles in the solid are not in special patterned positions. The fixed particles in these solids are every which way, not regular and orderly.

To keep our discussion of the scientific model of solids within reason, we shall refer only once more to solids in which the particles are disordered. We will confine the rest of our attention to crystalline solids, in which the particles are believed to be arranged in an ordered, regular, repeating manner.

5. *Many solids will melt.* It is easy to melt ice. It is a tricky business to melt sugar without scorching it, though it can be done. Salt will melt at a high temperature; liquid salt looks very much like water, but since it is hot enough to set a piece of paper on fire if the paper is quickly dipped in and out, no one knows how it tastes. Probably, if you had an asbestos tongue, you would observe that it tasted salty.
6. *Many solids will sublime.* *Sublime* is a special word; it means *to change directly to a vapor, or gas, from the solid state*. Solid carbon dioxide, known as Dry Ice, will sublime. A container filled with food and chilled with Dry Ice will stay cold as long as some Dry Ice is present. But after a while, as you know, the Dry Ice disappears. Instead of melting, it sublimates directly and becomes gaseous carbon dioxide, which then, like any other gas, diffuses away. Solids which have an odor usually have the odor because they

- sublime; naphthalene is an example. What do you think you would observe if you put a moth ball (naphthalene) under water?
7. *Some solids effloresce.* You would not think so from the word itself, but *effloresce* means to *lose water*. Sodium carbonate crystals ordinarily contain water; in a very dry climate this water is lost to the atmosphere. The crystals of sodium carbonate are fairly clear, looking a little like glass; when water is lost, they acquire a whitish appearance, somewhat like a flower. *Efflorescence* comes from a Latin word which means "to bloom like a flower." Efflorescence can be explained by Le Chatelier's Principle. If the water vapor pressure in the air is less than the water vapor pressure in the crystal, moisture tends to be given up by the crystal. When the water vapor pressure in the crystal equals that in the air, no further change occurs.
 8. *Some solids deliquesce.* This is the opposite of effloresce. For example, calcium chloride and sodium hydroxide will *pick up water from the atmosphere*. With sodium hydroxide the effect is striking. A pellet of solid sodium hydroxide will become liquid from the water it picks up. If you watch, you can see it dissolve itself in this water in several minutes. Only if the atmosphere is very dry will sodium hydroxide be unable to deliquesce. Deliquescence can also be explained by Le Chatelier's Principle. If the water vapor pressure in the air is greater than the water vapor pressure in the crystal, moisture tends to be absorbed by the crystal. When the water vapor pressure in the crystal equals that in the air, no further change occurs. Since you cannot tell without a lot of extra memorizing which solids will and which solids will not deliquesce, it is a good idea to keep all the lids on reagent bottles tightly closed when not in use.



Contrast the condition of each substance in the upper photo with its condition in the lower photo. What has happened to each?

10-2· BONDS IN CRYSTALS

Solid carbon dioxide will sublime under ordinary conditions. Salt will not; no one is surprised to find that a salt cellar that was filled last week is still filled a week later. Why does solid carbon dioxide change readily to a gas, while salt does not? Careful measurements of Dry Ice while it sublimates show that this solid absorbs energy when it changes from solid to gas. Some of this energy is used to separate one carbon dioxide molecule from others near it in the solid, so that the loosened molecule can escape as a gaseous molecule. The rest of the absorbed energy is used by the gaseous molecule to raise its temperature (and kinetic energy) up to the same level as the air molecules around it. (Solid carbon dioxide remains at a temperature of -78°C , just as ice remains at 0°C while melting in room-temperature surroundings.)

Measurements of the energy required to loosen up a crystal of salt, so that it, too, could sublime, show that a great deal of energy is required to separate the parts. We can conclude that sodium chloride, ordinary salt, does not sublime because the particles in the crystal are more tightly bound one to another than the much more loosely bound particles in solid carbon dioxide.

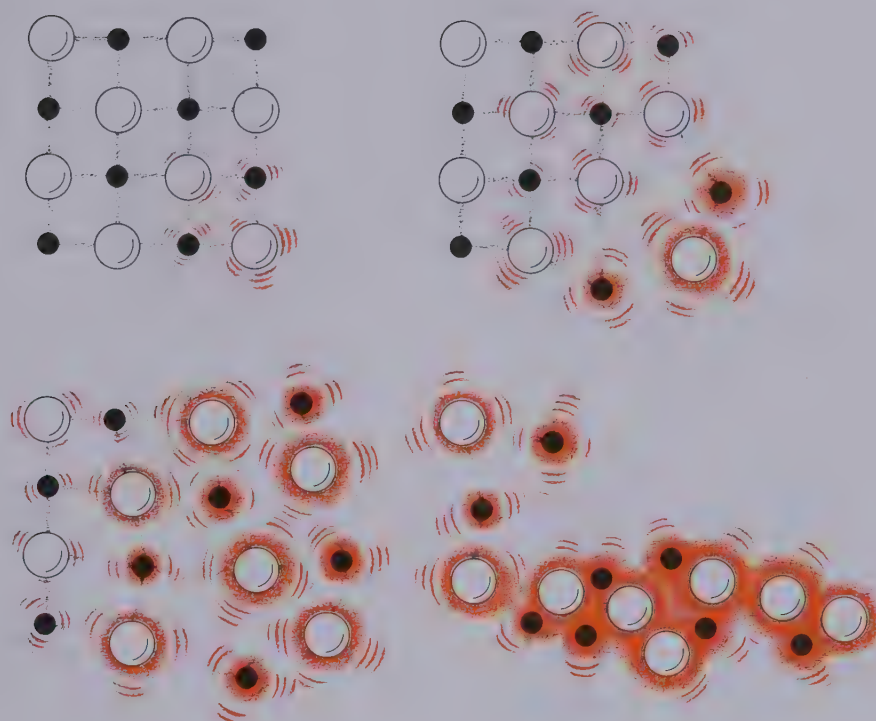
The same general picture can be applied to the melting of a solid to form a liquid. Sodium chloride melts at 801°C ; ice melts at 0°C . About five times as much heat energy is required to melt solid sodium chloride at 801°C as to melt an equivalent amount of ice at 0°C . Of the two, which has stronger bonds holding the particles in the solid together, salt or ice?

In thinking about the strength of the bonds holding the particles together in ice, in solid carbon dioxide, and in salt, we see that there are differences in the bond strengths. In Sec. 10-7 we shall use this information to help classify different kinds of solids. But now we can use this information to imagine what might happen when a solid melts. How does the model of a solid explain the process of melting?

10-3· THE MELTING OF A SOLID

In Exp. 2-3 you prepared heating and cooling curves for paradichlorobenzene. A number of questions were raised at that time which can now be examined further. As heat is added to a solid, each particle begins to vibrate more and more, back and forth about its position in a crystal. Continued addition of heat increases this vibratory motion even more. The increase in vibrations of the particles is indicated by the fact that the temperature of the solid rises. Finally, when the melting point is reached, the vibrations are so intense that the particles begin to separate from one another. The only energy required to pull them apart is the amount needed to overcome their forces of attraction. So once melting begins, no matter how much more heat we add, the vibrations do *not* increase. The addition of more heat simply supplies the extra bit of energy needed to break the restraining bonds between more particles. When this happens, each particle becomes separated from its neighbors and is free to move about in the liquid state.

There is no change in temperature while the solid is melting, because there is no increase in vibrations of the particles. But once melting is com-



How do the particles behave as a crystal melts?

plete and the substance has become completely liquid, addition of heat causes a further rise in temperature; the added heat now increases the motion of the liquid particles. This increased motion shows up as a rise in temperature.

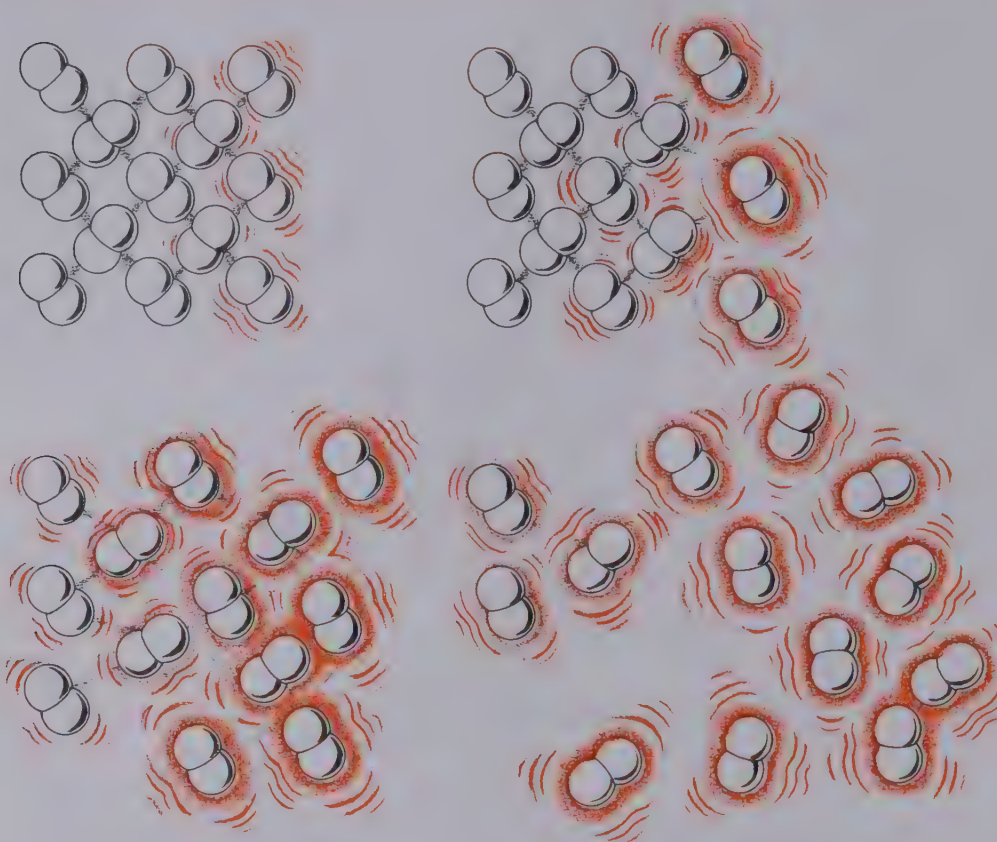
To summarize: Heat applied *before* melting begins increases the vibrations of the particles as indicated by a rise in temperature; *during* the melting process, the heat being applied is used to break the restraining bonds and free the particles. Since this heat does not increase vibrations, there is no temperature change; *after* melting is complete and particles are in the liquid state, addition of heat causes an increase in the motions of the particles, and this is indicated by a rise in temperature.

The melting point is the temperature at which there is no change in the vibration energy of the particles. At this temperature, the heat required per gram of solid to break the particles loose is called the *heat of fusion* (heat of melting).

For a mole of particles, the heat required is called the *molar heat of fusion*. The molar heat of fusion of sodium chloride is approximately five times greater than the molar heat of fusion of ice. How can this be? We shall learn the answer in Sec. 10-7.

10-4. THE SUBLIMATION OF A SOLID

The same general idea can be applied to the change of state from solid to gas. The *molar heat of sublimation* is the heat required when 6.02×10^{23} particles break loose from the solid and become gas molecules. Which would be greater for any solid, its molar heat of fusion or its molar heat of sublimation? We could guess correctly that the molar heat of sublimation is greater. Why?



A model for the sublimation of solid iodine.

For both fusion (solid becoming a liquid) and sublimation (solid becoming a gas) the same number of bonds in the solid must be broken and this takes a certain amount of energy. But, for the particles to become as free as gas particles would require still more energy than for them to be only as free as liquid particles are. Particles in liquids still attract each other somewhat because they are quite close together. It takes more energy to go from the solid to the gas state than from the solid to the liquid state. So, the heat needed to sublime one mole of solid is greater than the heat required to melt one mole of solid.

10-5· DYNAMIC EQUILIBRIUM, MELTING AND FREEZING, SUBLIMING AND CONDENSING

Suppose that we think of the reverse process, a liquid freezing or a gas becoming a solid. When a liquid freezes, the heat it absorbed to become a liquid is released. As we cool a liquid (imagine it to be water), the kinetic energy of the molecules becomes less and less; as the liquid gets still colder as more energy is removed, the molecules move so slowly that their attractive

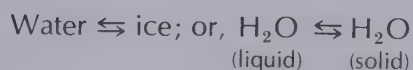
forces can hold them together to form little regions of ice. As more energy is removed, more liquid molecules lose energy, and the amount of ice grows. The temperature of the water-ice mixture remains constant although energy is released as water-water bonds are formed; the kinetic energy of the molecules remains the same, so the temperature does not change.

You will recall that during the melting process the temperature did not change; the added energy to melt the solid was used to break bonds in the crystal, not to increase the kinetic energy of the particles. As you have guessed, the unchanging temperature of melting is the same as the unchanging temperature of freezing. The freezing point temperature of water and its melting point temperature are identical, 0°C .



Note the size of the iceberg and then consider that most of it is submerged. Now consider how many moles of ice are in the iceberg and how many kilocalories of energy are involved in its melting or freezing.

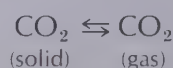
What would happen, according to this model, if we had a mixture of ice and water at 0°C and no heat was added to or removed from the mixture? Some of the water would freeze, releasing heat; and this heat would be absorbed by the ice, which would melt, forming exactly as much water as the amount which froze. Think of it this way: An innocent water molecule might happen to drift by a chunk of ice, to which it is attracted by the crystalline bonding forces. So the water molecule lodges in a comfortable spot on the solid ice and gives up its necessary amount of energy to the ice. The ice, to get rid of this energy, melts off one water molecule. The rate of freezing is the same as the rate of melting at 0°C for water. At 0°C , the water-ice system is in dynamic equilibrium. The equation that describes this is a double-arrow equation in which the double arrow signifies equal and opposite rates:



As we observe the system, we can observe no change in the total amount of liquid water and no change in the amount of solid ice. We would say from our observations at 0° C that water does not freeze and ice does not melt. But according to our model, they are freezing and melting at equal rates. The tendency toward minimum energy is exactly balanced by the tendency toward maximum randomness.

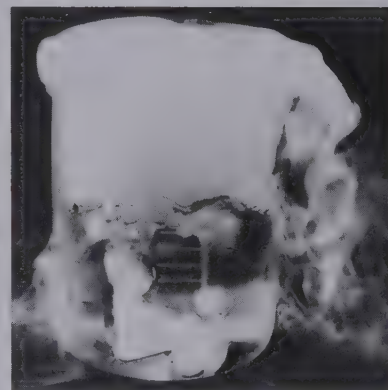
Above 0° C, water is a liquid. At these higher temperatures, the tendency toward randomness is stronger than the tendency toward least potential energy. Below 0° C, water is a solid (ice); the tendency toward minimum potential energy is stronger than the tendency toward randomness.

We can say the same sort of thing about sublimation. Dry Ice absorbs heat when it is put in room-temperature surroundings, and it sublimates because the tendency toward randomness is greater than the tendency toward minimum energy. At a lower temperature, about -78° C, solid Dry Ice and gaseous carbon dioxide are in dynamic equilibrium, if we put the system in a closed container so the gas cannot escape and heat cannot be absorbed by or released from the system. Under these conditions the dynamic equilibrium can be expressed by the equation:



For each mole of solid carbon dioxide molecules that sublime, one mole of gaseous carbon dioxide condenses to the solid state, in the same period of time. (Of course, for a mole of Dry Ice molecules to sublime will take a while. A mole of carbon dioxide molecules weighs about 44 grams, almost two ounces.)

It is interesting to check the prediction that can be made from our model with Dry Ice. A mole of carbon dioxide gaseous molecules will occupy a volume of 22.4 liters (about the size of a basketball) at 0° C and 760 torr. The temperature of the room you are in now is about 20° C, warmer than 0° C, so a mole of gas molecules will occupy more than 22.4 liters at this higher temperature. Also, chances are that the pressure of the atmosphere in your room is a little less than 760 torr (since you are probably not at sea level but at least a little higher). If it is about to rain, the pressure will be even less. At lower pressures, as you know, gases expand; so, the fact that the pressure is less than 760 torr also tends to make the volume occupied by a mole of gas molecules more than 22.4 liters. All in all, the model would predict that 44 grams of Dry Ice will sublime in the room where you are and occupy a volume somewhere around 30 liters. So, test the prediction. Get a balloon smaller than a basketball and stuff in about 44 grams (not quite two ounces) of Dry Ice. (Caution: Use gloves as it is hazardous to touch Dry Ice with the bare skin.) Tie the neck of the balloon tightly shut and wait.



10-6. THE STRUCTURE OF SOLIDS

The present scientific model for solids is able to describe their appearance as though we had a powerful microscope and could examine a solid with our own eyes. The properties we have studied here and evidence obtained from the way solids reflect x-rays have enabled us to arrive at this model.

Glass is a solid composed of a helter-skelter arrangement of silicon and oxygen atoms with a few other metal atoms tossed in, such as sodium, lead, and iron. What other solids that have an irregular arrangement of atoms can you think of?

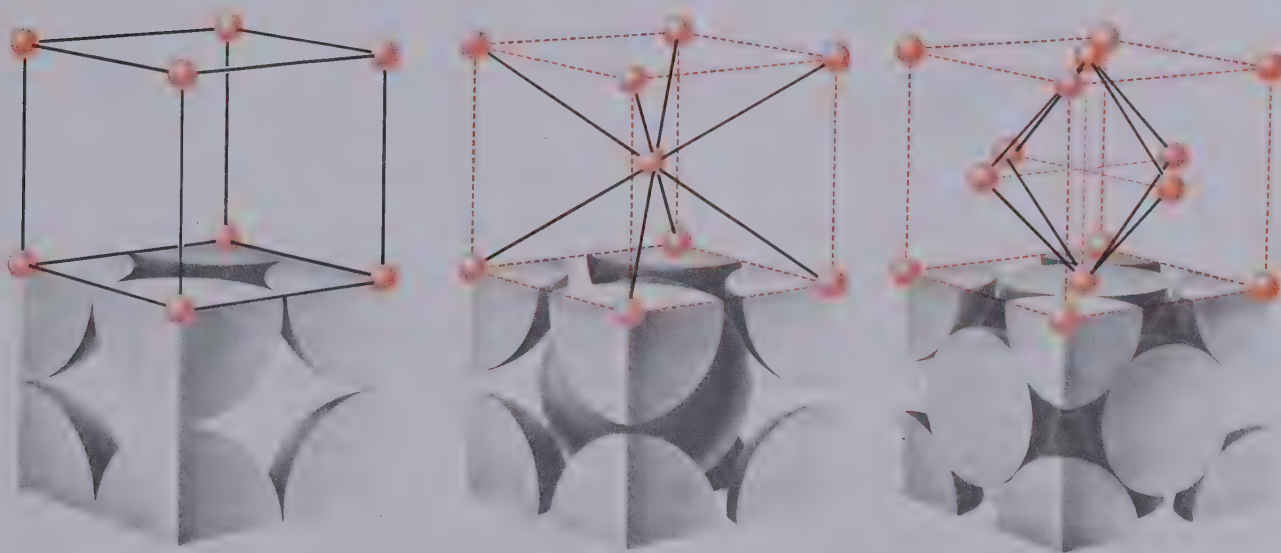
Many solids, such as sodium chloride, carbon dioxide, and ice, have regular structures. These regular structures are called crystals. A crystal is defined as a solid having a pattern of internal order which is repeated throughout the substance. For example, a chess or checker board is a flat surface with a repeating pattern that gives it internal order. A pile of these boards, with some space in between each, would be something like a solid crystal with a repeating pattern in three dimensions.

Crystals have various shapes. Thus, most salt crystals are little cubes, as you may know. The angles between the surfaces are 90° . These are not difficult to measure. You can construct a simple apparatus known as a *goniometer* and measure the angles of crystal surfaces for yourself. In fact, crystals can be classified in this manner, since all crystals of the same substance always have the same angles between corresponding surfaces.

A crystal is composed of units called *unit cells*. These determine the fundamental shape of the crystal and furnish a means for classification. Repetition of the unit cell produces the entire pattern, which is called the *space lattice*. The space lattice can be compared to the repeating pattern in wallpaper. The designer draws his pattern once in a small square or rectangle. This single drawing represents a unit cell. We can use the unit cell to represent crystal patterns, because this is the pattern which is repeated over and over to produce the crystal.

Types of Unit Cells

There are fourteen different types of unit cells recognized in the classification of crystals, but we will consider only three of the most common ones. The first is a simple cube; each point at the corner of the cube is a *lattice point*,



(From left to right) Cubic, body-centered cubic, and face-centered cubic unit cells.

where an ion, atom, or molecule is located. Closely similar to this arrangement is a *body-centered* cube. This type of unit cell has a particle at nine lattice positions, one at each corner of the cube and also one in the middle. The particle in the center is surrounded by eight other particles. This is a loose arrangement, and substances with this structure are less dense than those having closer-packed particles.

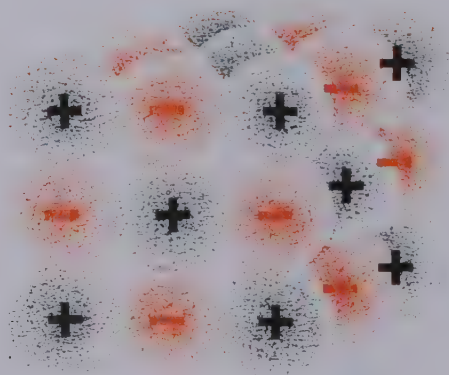
The third type of unit cell is the *face-centered* cubic arrangement. In this cell each particle is surrounded by twelve other particles. There is a particle at each corner of the cube and one in the middle of each side. This results in a more compact pattern, and substances having such an arrangement are more dense.

10-7. CLASSIFICATION OF SOLIDS

It is also useful to classify solids on the basis of the kind of particle which occupies the lattice points. Using this method of classification, there are four types of crystals: (1) ionic, (2) molecular, (3) network, and (4) metallic. The kind of bonding determines the type of solid.

Ionic Solids

The particles that occupy the lattice points in an ionic solid are positive and negative ions. In the sodium chloride crystal, half of the lattice points are occupied by sodium ions, Na^+ , and half are occupied by chloride ions, Cl^- .



A model of an ionic solid.

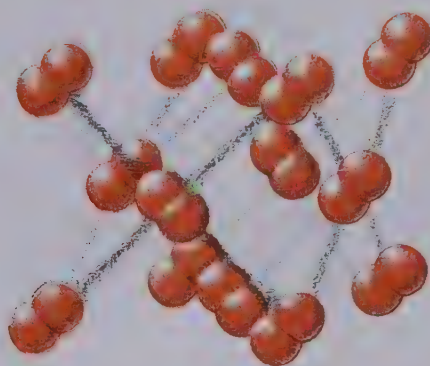
The force of attraction between such particles is great, and this determines their properties. Ionic solids have a high melting point and tend to be hard and brittle. Since the ions are not free to move about, these solids are non-conductors of electricity, although when such solids are melted or dissolved, the ions are free to move and are good conductors.

From what we know about the high melting point and large molar heat of fusion of sodium chloride, we can now conclude that the ionic attracting forces in ionic solids are very strong. That is, when you have a solid which

is composed of charged particles, positive and negative, in a regular repeating pattern, that solid will have a high melting point; it will be hard and brittle at ordinary temperatures, all because of the strong ionic bonds within the solid.

Molecular Solids

Molecular solids are those in which the lattice points are occupied by molecules. The bonding *within* each of the molecules is covalent. The bonding *between* the molecules is due to either van der Waals forces or polarity. Elements in the upper right of the periodic table tend to form molecular crystals bound by van der Waals forces. Examples are nitrogen, oxygen, and sulfur. Elements that form molecules in which each atom acquires the noble gas configuration are held together by van der Waals forces. Water and carbon dioxide are examples of compounds in which the molecules are held together by polar bonds.



A model of iodine, a molecular solid.

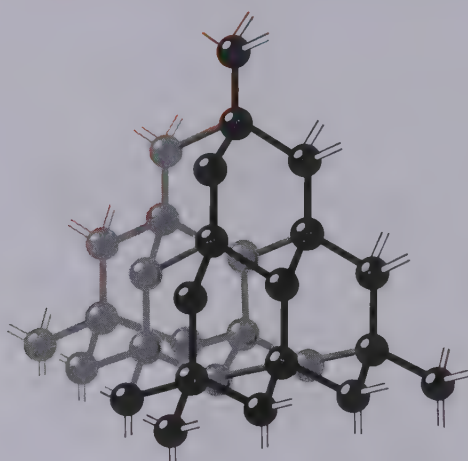
We will learn more about the structure of ice in Sec. 10-8. But let us take another look at the structure of solid carbon dioxide. At each lattice point there is a molecule of CO_2 . What holds one of these molecules in place with respect to the neighbors next to it? What is the nature of the force?

We can guess correctly that the force is not ionic since we already know that carbon dioxide, as a solid, sublimates at ordinary temperatures, but solid ionic crystals, such as salt, do not. The forces in solid carbon dioxide must be weaker. The model used here points out that the difference in the electronegativity of carbon and oxygen atoms is great enough to cause the bonds to be polar covalent. This difference suggests that in the carbon dioxide molecule each oxygen atom is slightly negative, and the carbon atom is slightly positive. It is the negative-positive-negative attractions that hold the carbon dioxide molecules in place in solid carbon dioxide. However, since each part is only slightly charged, not fully charged as an ion is, the force is weaker.

In molecular solids, such as ice, solid carbon dioxide, and sugar, the force which holds the particles in the crystal is a positive-to-negative kind of force which is rather weak compared to the force of attraction in an ionic solid.

Network Solids

Network solids are different. In a network solid each lattice point is occupied by an atom, rather than a molecule or an ion. Each atom shares electrons with its neighboring atoms, and they with it. Each neighbor atom has other neighbors on the other side with which it shares electrons. In a network solid each atom is bound directly or indirectly to every other atom by covalent bonds. The result is a very strong, hard substance.



A model of diamond, a network solid.

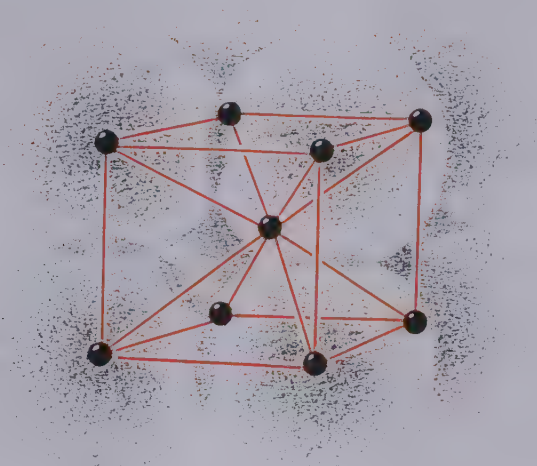
Diamond is an example of a network solid. As you know, diamonds are very hard. We would expect this, now that we know that diamond is a network solid. Actually, of course, it really happened the other way around. Man knew that diamond was hard and over hundreds of years tried to imagine a model that would explain why it was hard. Now we have a model which does, although whether or not it is right is a question.

One test of the "correctness" of a model is its predictive power. For example, if diamond is hard for the reasons given, then from what we know about the elements and the periodic table, we could predict that the compound silicon carbide, SiC , would be a network solid. It, too, would be predicted to be hard. As it turns out, this prediction is correct. Silicon carbide is almost as hard as diamond, and much less expensive. It is used in industry as an abrasive and called carborundum. What would you guess is the melting point of carborundum? Using your knowledge of the periodic table, predict other elements which might form network solids. Check your predictions by using a reference source.

Metallic Solids

All metals except mercury are solids at room temperature. Mercury becomes a solid at temperatures below -39°C , its melting-freezing point. Loosely speaking, metallic solids are a kind of combination of ionic and network solids. That is, each lattice point is an ion, a metal atom that has lost one or perhaps a few more electrons. However, the lost electrons are still in the crystal, bouncing around almost like gas molecules inside a container.

Now, if each lattice point is a positive ion, and that were all that there was in the crystal, we would expect it to fly apart from the positive-positive repulsions. It is the free, loose, almost constantly moving electrons that add the binding which exists to make the ions at the lattice points stay together.



A model of a metallic solid.

At any given instant, one or more electrons are between and among almost every two or three positive metal ions. In the next instant, those electrons will be somewhere else in the crystal doing their thing, and other electrons will take the place of the ones that just left. Overall, according to the model, there is a positive-ion-to-negative-electron kind of attraction which holds the crystal together.

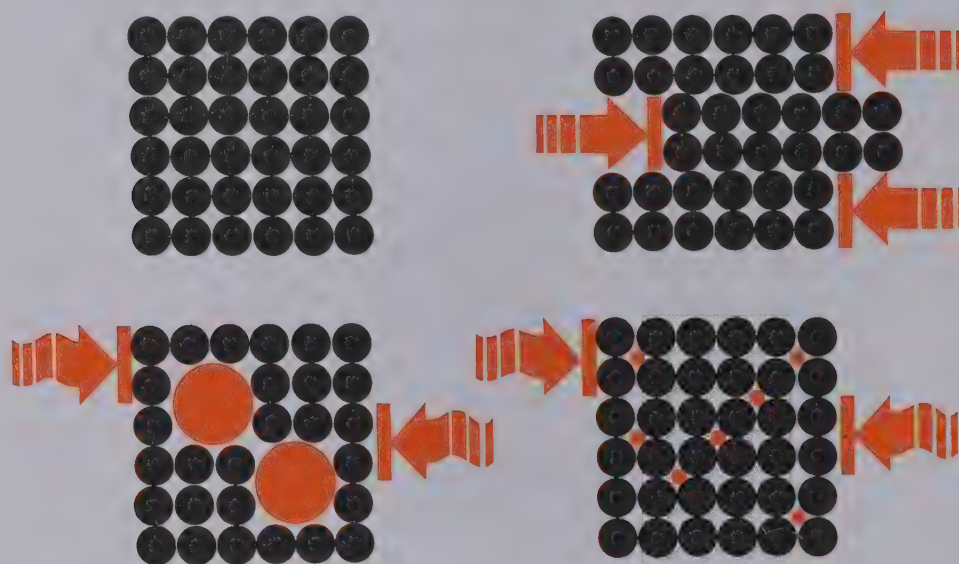
What about the force? How strong is it? You can suspect that with all this batting about of electrons, with some metals having lattice points that are single-charged positive ions and other metals with more highly charged positive ions, you would have some metals with weak forces holding the crystal together and some with strong forces. This is, indeed, the case. As you know, some metals, such as lead, are soft. The forces in mercury are so weak that it is a liquid at ordinary temperatures. Other metals are hard, such as chromium and tungsten.

It may surprise you to learn that iron is a soft metal. Most people think of it as hard. Steel is, indeed, hard, especially if it is tempered. But steel is only partly iron; the other constituent of steel always includes some carbon, and

often still other substances. The presence of these added atoms makes iron into steel, which is hard. That is, we can think of a piece of pure iron as a crystal, with rows upon rows of ions like little balls, one on top of the other.

The forces of attraction, from the presence of the loose electrons, are strong enough to hold the ions together. You cannot pull them apart. Of course, even if you don't pull them apart, you could slide one layer over another. This is what happens when you bend a copper wire, or hammer on a piece of thicker metal, to make it thinner.

But what if, instead of each ion in the layer being the same, there was, every once in a while, a bigger ion? You can see from the illustration that it is now going to be more difficult to slide one layer over another.



Or what if, every once in a while, there is a small ion, sort of out of place, between the bigger ions? This, too, would make it more difficult to slide one layer over another.

Iron becomes harder, as steel, by the addition of these kinds of "extra" particles. Gold is another very soft metal. To make it hard enough to be used as jewelry, copper is added. Or nickel might be used. Nickel mixed with gold makes it "white," not yellow; so the alloy, the mixture of gold and nickel, is called "white gold."

10-8. THE STRUCTURE OF LIQUIDS

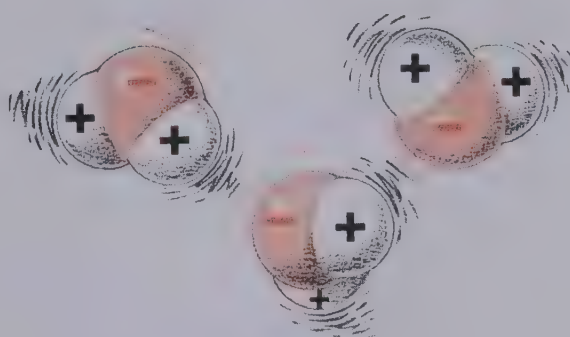
In this chapter we are eventually going to study what happens when a solid dissolves in a liquid. Now that we know about the structure of solids, we can turn our attention to liquids. What is a liquid? How does it differ from a solid? What is the model for a liquid like?

As you know, the kinetic model suggests that a liquid is composed of particles, molecules or atoms (usually molecules), that move around every which way bumping into each other, some moving very fast, some slow, some at

medium speeds, going faster or slower after a collision than before the collision, and so on. The model also suggests that the liquid particles are held together as a liquid by some kind of force. There are different kinds of liquids—ionic, metallic, and molecular—and in each the nature of the force is a little different. To keep things as simple as possible, we will look only at the model for molecular liquids, since they are most commonly found in everyday life. Water, gasoline, and alcohol are molecular liquids.

First, let's look at gasoline. Ordinary gasoline is composed of a mixture of different molecules, and each molecule is itself composed only of carbon and hydrogen atoms. The different kinds of molecules are different because the number of atoms in each is different. Thus, one of the most common molecules is nonane, C_9H_{20} ; another is octane, C_8H_{18} . The electronegativity of carbon and of hydrogen differs by only 0.4. This means that these molecules are only slightly polar; there is a little positive-to-negative attraction between and among nearby nonane or octane molecules. We would expect that the molecules in liquid gasoline would evaporate, to form a gas, very easily. This is correct.

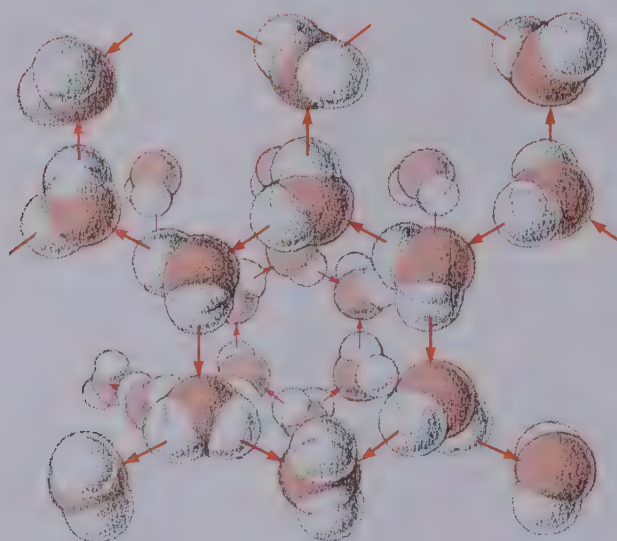
Next, let's look at water, which is composed of hydrogen and oxygen atoms. The difference in electronegativity between hydrogen and oxygen is 1.4. We would expect that in a water molecule the oxygen, with an electronegativity of 3.5, would be clearly negative and each hydrogen, with an electronegativity of 2.1, would be distinctly positive. A picture of water molecules might look something like this.



A model for liquid water.

Water requires much more energy to become a gas than we might predict. The water molecules are held together by a fairly strong force. In the drawing the artist has drawn shimmery lines to suggest artistically the forces of attraction (hydrogen bonds) between molecules.

As water gets colder, the force becomes more effective. The hydrogen bonds increase in number as the water molecules slow down while the temperature of the water drops. In fact, as water freezes to ice, a whole network of hydrogen bonds develops, holding the water molecules in place, with large empty spaces, as you can see in the artist's sketch of an imaginary sheet of ice at the top of the next page. (Ice is really a network of water molecules fastened one to another by hydrogen bonds in three dimensions.)



A model for a very common molecular solid.

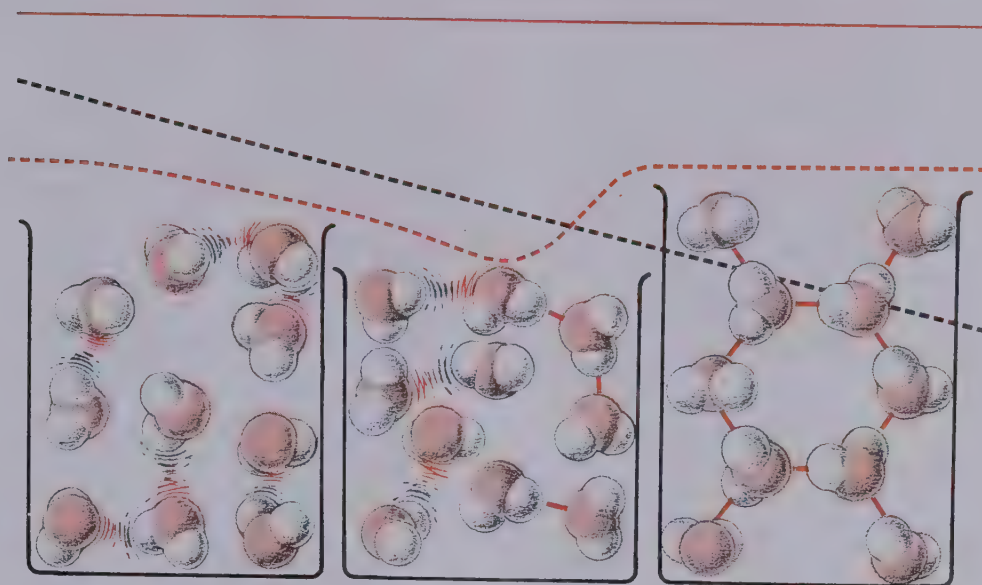
Not as many of these open spaces exist in liquid water as in ice. As liquid water freezes, it expands because many more of these empty spaces are formed by the hydrogen bonds holding water molecules in position. A gram of water occupies a volume of approximately one cc, as you know. A gram of ice occupies a larger volume. The density of water is about 1.0 gram per cc; the density of ice is about 0.9 gram per cc.

As water at room temperature cools, the molecules do not move around as much; the volume of liquid water tends to shrink a little; more hydrogen bonds form between and among nearby water molecules, with empty space developing here and there in the clusters of water molecules. But this effect tends to make the water expand a bit as it cools! So, as water cools, there are two effects that are opposite in their results. For water cooling a little from room temperature, the reduced molecular motion effect predominates, so water shrinks a little. As we cool it still further, it continues to shrink for the same reasons, but not quite as much. After all, the colder it gets, the more effective the hydrogen bond build up becomes with its empty spaces in between and among water molecules.

An analogy can help you visualize these opposing processes. Imagine that you place a strong magnet at the edge of an inclined board. Then imagine that you roll an iron ball down the incline at a high speed. There would be little chance for the ball to be permanently attracted to the magnet, because it moves past too rapidly. However, if you imagine the same ball rolling down the incline very slowly, the chances of its becoming attached to the magnet become much greater. So it is with water molecules. An electrostatic positive-negative attraction exists between the hydrogen atom in one molecule and the oxygen atom in another molecule. The more slowly the molecules move, the more effective this attraction becomes in forming hydrogen bonds.

Below 4°C , the effect of hydrogen bonding predominates; above this temperature, the effect of increasing kinetic energy is dominant.

As the water gets colder and colder, the shrinking effect begins to lose out and the expanding effect begins to take over. Below 4°C , as water cools still further, the expanding effect predominates. So, at 4°C , water is as shrunk as it can get; it has a maximum density, as you learned in Chapter 3. Then when the liquid water at 0°C freezes to ice, it expands as fully as possible, with the least density it can have, as ice.



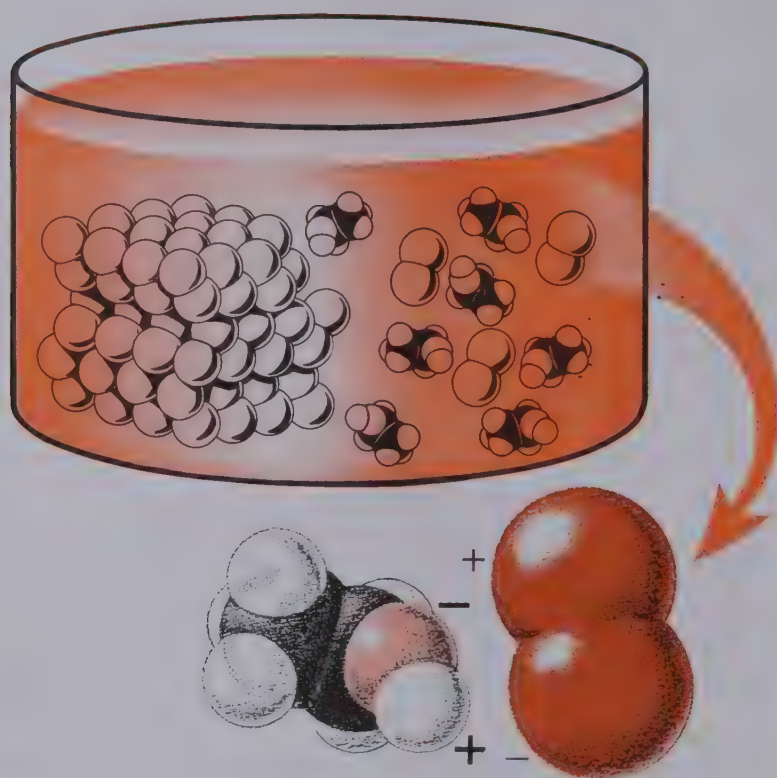
How do the molecules of water behave as the temperature of the water drops?

10-9. THE DISSOLVING OF SOLIDS IN LIQUIDS

Iodine will dissolve in liquid carbon tetrachloride; it will also dissolve in alcohol. Tincture of iodine is a solution of iodine in alcohol, and is sometimes used as an antiseptic for cuts. It is rather caustic and damages not only bacteria, but skin as well. What happens when iodine, a molecular solid, is dissolved in alcohol?

Not much energy is required to pull iodine molecules apart from each other in the solid crystal, since it is a molecular solid. There is a small, very weak, attractive force between an iodine molecule and an alcohol molecule. This force is due to the slight electrical charge that exists on an alcohol molecule because of the small electronegativity difference between carbon and hydrogen. So, as an alcohol molecule approaches an iodine crystal, the slightly positive hydrogen of the alcohol molecule attracts, very slightly, the electrons of the iodine molecule, and the iodine molecule is pulled off, away from its nearby iodine molecules in the crystal. The molecular bond that held the iodine molecule in place in the crystal is broken. This requires only a little energy. The new molecular bond formed between the dissolved iodine molecule and

the alcohol molecule releases only a little energy when it is formed. Give or take a little, about as much energy is needed to break the old bond as is released when the new bond is formed. So, iodine dissolves in alcohol.



A model for the dissolving of iodine in alcohol.

Iodine dissolves to a slight extent in water, for about the same reason. As a water molecule, with a much greater separation of positive and negative charge, approaches an iodine molecule in a crystal, a bond between the water molecule and the iodine molecule is formed. However, this bond is weak because the iodine molecule itself has no positively or negatively charged ends, and the attraction is to the electrons of the iodine molecule. Iodine forms weak bonds with alcohol for the same reason. The energy required to break the molecular bond in the crystal is about equal to the energy released when the new bond is formed between the dissolved molecule and the water.

Sugar dissolves a little bit in alcohol and even better in water. Sugar is a molecular solid, with weak bonds holding each sugar molecule in place. But sugar molecules are composed of carbon, hydrogen, and oxygen. The large electronegativity difference between hydrogen and oxygen means, for sugar, that some of the hydrogen atoms in its molecule are distinctly positive, compared to the negative oxygen to which they are attached. Therefore, one

sugar molecule in a crystal attracts its neighbors more strongly than was the case for iodine.

More energy is required to break a sugar molecule loose from a crystal than was needed for iodine. When we try to dissolve sugar in alcohol, only a little energy is released by the sugar and alcohol molecule as they go off, hand in hand. That is, the positive-negative charge on the alcohol molecule is not much, so the bond with the pretty good positive-negative part of the sugar molecule is not too strong.

But with water, we have a different result. The water, like the sugar, has hydrogen and oxygen atoms in its molecule. We could expect a hydrogen bond to be formed between water molecules and a sugar molecule. The formation of those hydrogen bonds, as a sugar molecule dissolves and goes off hand in hand with several water molecules, can be expected to release much more energy than for the similar case when sugar dissolved in alcohol. We expect to find that sugar is much more soluble in water than it is in alcohol, and this is true.

Salt, an ionic solid, will not dissolve in alcohol at all. As you know, it dissolves in water rather well. Salt will not dissolve in alcohol because it is an ionic solid and a great deal of energy is required to pull an ion away from its oppositely charged neighbors in the solid crystal. The little bit of energy released when an ion of sodium or chlorine would go off hand in hand with an alcohol molecule is too small to have any effect. But, when one of these ions goes off with water molecules, a great deal of energy is released. Energy is released that is about equal to the energy required to break the ion loose from its crystal. Each sodium or chloride ion is surrounded by five or six or more water molecules, bonded to it by the positive-negative attractions. The ion has a clearly identifiable charge; the water molecules each have a partial positive and partial negative charge; the energy released is significant.

Silver chloride is another ionic solid. It will not dissolve to any real extent in water. The reason can almost be guessed: More energy is required to break the ions loose from the crystal than is released when the ions join up with a bunch of water molecules. Sodium chloride is composed of sodium ions and chloride ions, in the solid crystal. Silver chloride is composed of silver ions and chloride ions, in the solid crystal. If both would dissolve in water, we would have the ions attached to water molecules batting around in solution. As it is, sodium chloride will dissolve and silver chloride will not dissolve in water. Silver chloride will not dissolve, because it requires much more energy to break silver ions loose than it does to break sodium ions loose from their crystalline structure. From this, we would predict that silver chloride is a harder solid than is sodium chloride, and this turns out to be correct.

Let us think about the reverse process. Suppose that we had a few sodium ions and a few chloride ions in solution already. Would they tend to form a solid and not dissolve? Of course not. They would tend to stay in solution. But suppose that somehow we were able to get silver ions and chloride ions together, in solution. What would happen? We would predict that heat would be released as the silver and chloride ions joined together to form solid, undissolved silver chloride. Heat is expected to be released because the bonds

in solid silver chloride are much stronger than the bonds the silver and chloride ions have with water molecules.

Sodium chloride dissolves because the tendency to maximum randomness overcomes the tendency to minimum energy. Besides, not too much energy is required to break up the solid sodium chloride. To break up solid silver chloride and get it to dissolve requires much more energy. The result is that for solid silver chloride the tendency to minimum energy is greater than the tendency to maximum randomness. The same is then also true for silver ions and chloride ions in solution. They tend to get together in an ordered way, as a crystalline solid, releasing energy to do so. Sodium and chloride ions in solution, on the other hand, tend to stay in solution; for them the tendency to randomness is greater than the tendency to lose energy by forming an orderly crystalline solid.

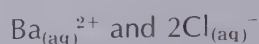
All substances tend to dissolve, to get into a condition that is more random. But, unless the energy that is needed is small, or unless the larger amount of energy that is needed (for sodium chloride or silver chloride) can be somehow supplied, the tendency to minimum energy wins out over the tendency to maximum randomness. So much energy is needed for silver chloride to dissolve that it cannot be supplied by the new bonds that would be formed in solution.

10-10. IONIC EQUATIONS

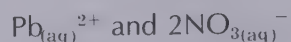
How can you tell what to write in an equation for each reaction that you will observe in Exp. 10-3?

First, note that all of the solutions in Exp. 10-3 are solutions of ions. For example, the solution of barium chloride, BaCl_2 , contains barium ions, Ba^{2+} , and chloride ions, Cl^- . So, you need to know more about the ions. The names of the ions and the formula for each ion that you will use in Exp. 10-3 are listed in the lab manual.

To identify the ions present in a solution of BaCl_2 , find barium and chlorine in the table and notice the formula for the ions, with their charge. In this case you find Ba^{2+} and Cl^- . Notice the double positive charge on the barium ion and the single negative on the chloride ion. To make the positive and negative charges add up to zero, we need two chloride ions, 2Cl^- , for each double positive barium ion. So, to describe the ions in a solution of barium chloride in water we write:

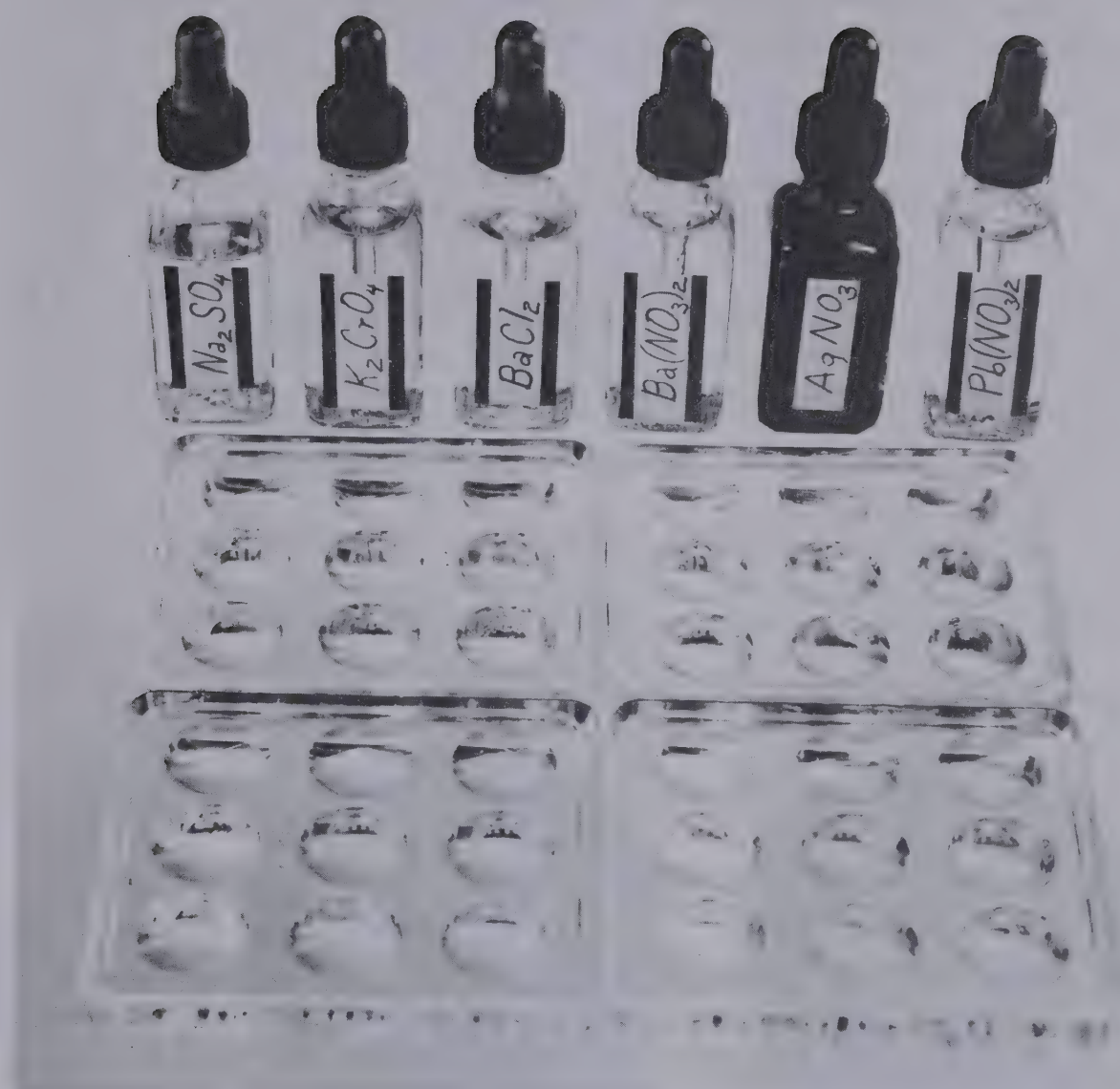


The subscript "(aq)" comes from the Latin word for water, *aqua*, and indicates the ions are in a water solution. The barium chloride solution was mixed with a solution of lead nitrate in water. For it we get the information from the table and write:



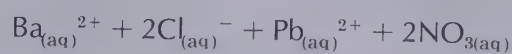
Now, in the laboratory, you will mix the two solutions, and chemists use a plus sign to symbolize that one was added to the other:





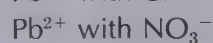
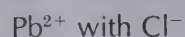
A way to arrange the materials for doing Experiment 10-3.

To save time, chemists use a plus sign instead of "and," so we now have this set of symbols to indicate that the two solutions of ions were mixed:

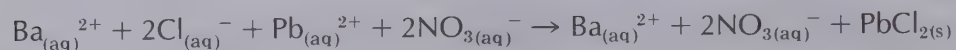


When they are mixed, something happens; a white precipitate forms. This precipitate forms because it is insoluble, or almost so. The heat energy released as the ions build up into a solid crystal comes from the ionic bond energy. That crystal does not dissolve, because more energy is required to break those ion-ion positive-to-negative attractions than is available. So, when those ions are present in the mixed solution, they form the solid crystals as a white precipitate.

The question is, which ions do this? It cannot be anything but some positively and some negatively charged ions; two ions of the same charge do not attract each other. We have these positive and negative possibilities in the mixed solutions:



Two of these can be eliminated. We know that barium ions and chloride ions are soluble, since we used a barium chloride solution. So, for barium chloride, the energy needed to pull apart the ions in a crystal is not too great. We know that barium chloride dissolves. The same for the lead and the nitrate ions; lead nitrate dissolves in water. Therefore, it must be either the lead and chloride ions or the barium and nitrate ions. One of these two equations is correct, the other one is incorrect:



The subscript "(s)" stands for *solid* and indicates a precipitate.



Crystals of silver nitrate and sodium chloride were placed in distilled water in the petri dishes. What happened?

You can figure out from your observations which of the two choices is correct for all the parts of Exp. 10-3. There will always be four possibilities; two of these can be eliminated easily and one of the other two deduced from your observations in the laboratory.

Coming up in the next chapter is an enjoyable part of chemistry that was promised at the end of Chapter 8. Now you can apply your knowledge to the question: What is the unknown substance present in my solution?

Suggestions for Creative Work

1. Devise an experiment to determine the melting point of glass.
2. Investigate the structure of one of the types of crystals and construct a model of its unit cell from Styrofoam spheres.
3. Grow large crystals of one or more substances; construct a goniometer and measure the angles which help to determine the system to which the crystal belongs.

Suggestions for Creative Writing

1. Write a paper discussing the things you have learned in chemistry which will enrich your daily activities, even though you may not plan to take more science.
2. Apply your ability to use the methods of science by reading several authoritative articles, pro and con, on a given subject. Then write a paper to defend your own position on the subject.

Practice Exercises *(Answers on p. 323)*

1. State three general properties of solids, and apply the kinetic theory and the principles of bonding and intermolecular forces to explain why solids exhibit these properties.
2. Apply the tendencies toward minimum energy and maximum randomness to explain the melting of ice.
3. Predict whether the following solids will be ionic, molecular, or metallic: (a) I_2 , (b) CO_2 (Dry Ice), (c) $CsCl$, (d) Fe , (e) LiF .
4. Define the term "unit cell" and illustrate three different types of cubic unit cells.
5. Define deliquescence and name one solid that exhibits this property. Name one practical application of this property.
6. Using the effects of hydrogen bonding and kinetic energy, explain why water is most dense at $4^\circ C$.
7. Write the ionic equations for the reactions that are expected to occur when the following sets of solutions are mixed:
a. $BaCl_2 + AgNO_3$ b. $Na_2CO_3 + Pb(NO_3)_2$ c. $(NH_4)_2S + NiCl_2$
8. (Multiple Completion; see special directions in Appendix 13)
The following substances are classed as network solids
 1. diamond
 2. silicon carbide
 3. graphite
 4. copper

9. (Multiple Completion; see special directions in Appendix 13)
Ions that would be expected to form precipitates with Ag^+ are
1. $\text{C}_2\text{H}_3\text{O}_2^-$
 2. Cl^-
 3. NO_3^-
 4. CrO_4^{2-}

Self-Test (Answers on pp. 323, 324)

1. Why do the crystals of N_2 , O_2 , and F_2 have low melting points?
2. Assume that you have samples of the following solids: NH_3 , Na, KCl, H_2O , Ar, and Si. Which of these would be the *best* example of:
 - a. High degree of hydrogen bonding?
 - b. Good electrical conductor?
 - c. Van der Waals forces mainly responsible for holding it together?
 - d. Contains covalent bonds and has high melting point?
3. Apply the principles of bonding, intermolecular forces, and kinetic energy to explain why solids have these properties: (a) definite shape, (b) poor ability to diffuse, (c) ability to form crystals.
4. State whether the following solids are ionic, metallic, molecular, or network solids.

a. Al	d. Si
b. CaCl_2	e. CO_2
c. iodine	f. Na_2SO_4
5. Apply Le Chatelier's Principle to explain why calcium chloride is deliquescent.
6. Sketch a body-centered unit cell.
7. Explain the changes in energy and order in a solid as it melts.
8. Discuss one method for preparing crystals used in Exp. 10-1.
9. Write ionic equations for the reactions that are expected to occur when the following sets of solutions are mixed:

a. $\text{BaCl}_2 + \text{Na}_2\text{SO}_4$	b. $(\text{NH}_4)_2\text{S} + \text{CoCl}_2$	c. $\text{AgNO}_3 + \text{K}_2\text{CrO}_4$
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10. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION

Dry Ice (solid CO_2) is classed as a molecular solid

REASON

Because the lattice points are occupied by molecules.

Bibliography

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A fine book on the art of growing crystals, systems of crystals, and the importance of imperfections.
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A short discussion of the relationship of chemistry to geology. The new theory of decompression accounts for the crystals of quartz and silicon dioxide.

Holden, Alan, and Phylis Singer, *Crystals and Crystal Growing*, Anchor Books, Doubleday & Company, Inc., New York, 1960.

One of the most comprehensive books on crystal structure and how to grow crystals. Contains many illustrations and photographs. Several recipes are included. Paperback.

Livingston, R. L., "The Teaching of Crystal Geometry in the Introductory Course," *J. Chem. Ed.*, July 1967, 376-383.

An excellent presentation of unit cells along with cubic, body-centered, and face-centered arrangements. Many diagrams. Such crystals as diamond, graphite, and sodium chloride, along with many others, are discussed. Recommended for all students.

Parsons, Cyril, and Clare Dover, *The Fundamental Materials*, Ginn and Company, Boston, 1966.

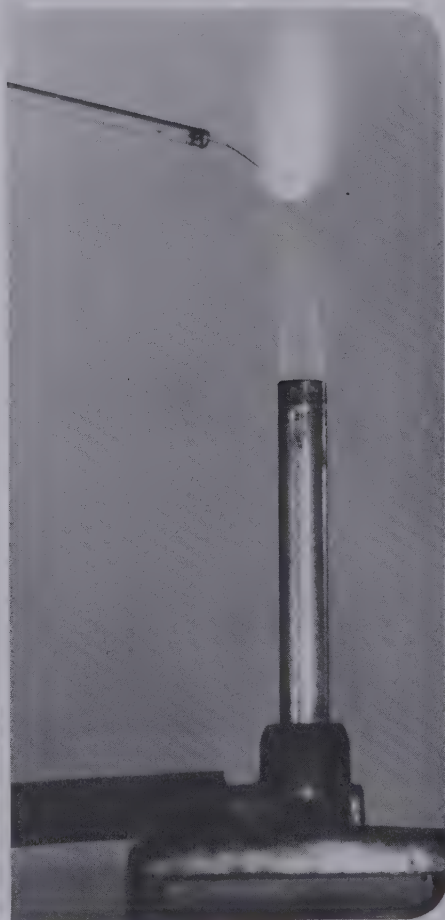
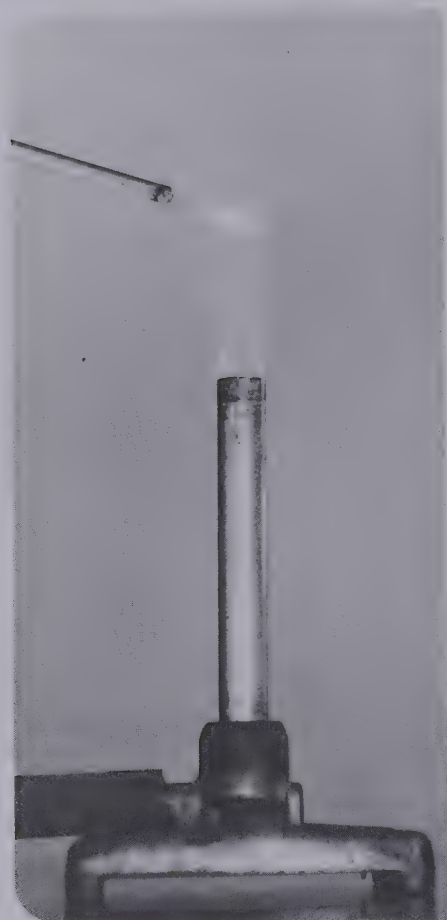
The section on crystals and their structure is outstanding. Colored photographs and illustrations.

Wohlrabe, Raymond A., *Crystals*, J. B. Lippincott Co., Philadelphia, 1962.

Discusses the architecture of crystals, how to grow them, and their uses in industry and electronics.

Wunderlich, Bernhard, "How Big Molecules Crystallize and Melt," *Chemistry*, October 1966, 8-13.

The thermodynamic influence upon crystals and their structure is emphasized. Diamond, graphite, methane, and polyethylene are among those included.





AN INTRODUCTION TO QUALITATIVE ANALYSIS

OBJECTIVES:

By the time you have completed your study of Chapter 11, you will be expected to demonstrate acceptable performance on the following objectives.

1. *Identify* the cation and anion in a salt solution, given the “unknown” solution and a procedure to follow.
2. *Recognize* the cation in an “unknown” salt solution, given the group test results and the results of at least one confirmatory test.
3. *Recognize* the anion in an “unknown” salt solution, given the group test results and/or the results of one confirmatory test.
4. *Explain* two functions of the Na_2CO_3 solution after the cation has been identified.
5. *Explain* the chemistry of the chloride test.
6. *Explain* the chemistry of the bromide-iodide test.
7. *Cite* at least one example of the use of the common ion in qualitative analysis.
8. *Cite* at least one example in which the principles of chemical equilibrium are applied in qualitative analysis.
9. *Explain* the function of HCl in the Group II test for cations.
10. *Explain* the function of NH_4Cl in the Group IV test for cations.
11. *Write* balanced chemical equations for any reaction, given the reactants.

SUGGESTED ORDER OF STUDY:

1. Study Secs. 11-1 through 11-5.
2. Review the principles of precipitation (Exp. 10-3).
3. Review the principles of acid-base reactions (Chapter 4 and Exp. 4-4).
4. Review cation and anion tests (Exps. 5-2, 6-5, 6-6).
5. Identify the cations and anions in the “unknown” salt solutions provided by your instructor.
6. Do the Practice Exercises and review.
7. Take the Self-Test and review as needed.
8. Take the test on Chapter 11.

11-1. PRINCIPLES OF QUALITATIVE ANALYSIS

We come now to a summarizing unit in our survey of chemistry. *Qualitative analysis* is a procedure for determining what substances are present in an unknown material. In the procedure we will follow, you will identify positive ions (*cations*) and negative ions (*anions*) in a water solution. The purpose of this unit is two-fold: (1) to introduce you to an interesting and important area of chemistry and (2) to apply in a practical way the principles and concepts you have learned. Differences in solubility, the principles of ionic theory, hydrolysis, the common ion, buffers, and acid-base reactions become most important. Knowledge of atomic structure and equation writing are all involved and are tools as essential to successful laboratory work as the test tube. Other students have found this unit extremely interesting, because an air of excitement and suspense pervades their attempt to identify unknown compounds. It also helps to present a unified picture of the field of inorganic chemistry.

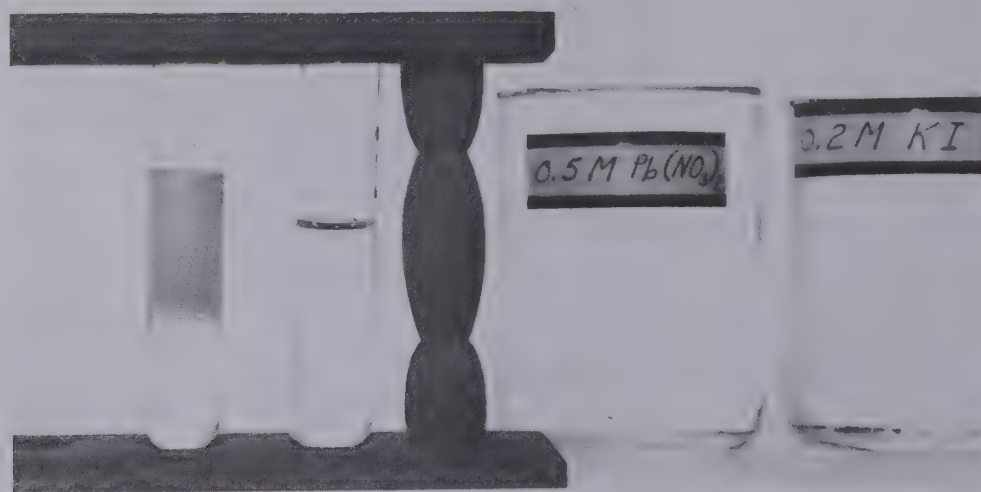


Some typical equipment needed for doing qualitative analysis.

The unknowns you will be asked to identify are water solutions of ionic compounds. Positive and negative ions are identified separately by using a systematic pattern of tests. Our procedure is based upon precipitation of these ions by the addition of reagents which produce compounds of varying solubility.

Precipitation

An understanding of the solubility rules is necessary to intelligent laboratory work. Otherwise, it becomes a matter of following a “cook-book” recipe without knowing what is happening or why it happens. A continuing review of the principles of precipitation, which you discovered in Exp. 10-3, is recommended as you work on qualitative analysis.



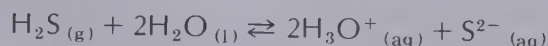
The formation of a precipitate in a test tube.

The varying solubilities of metallic chlorides, hydroxides, sulfides, and carbonates permit us to classify metallic ions into six groups. The presence of ions in each of the groups is detected by means of *selective*, or *group*, tests. Once a positive test for a group is obtained, we use *specific*, or *confirmatory*, tests to identify which particular member of that group is present in the unknown solution.

A similar plan is used for identification of the nonmetallic ions. These are classified into four groups. Precipitation plays an important part in their positive identification.

Buffers and the Common Ion

The common ion effect is applied in various ways in qualitative analysis. Small changes in the pH of a solution have a considerable effect on precipitation. Hydrogen sulfide, H_2S , is a weak acid which reacts with water to form some hydronium ions and sulfide ions: It is one reagent used to separate metallic ions into groups.

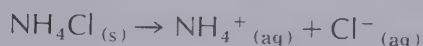
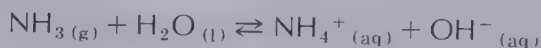


The subscripts on the formulas indicate that H_2S is a gas (g); that H_2O is a liquid (l); and that H_3O^+ and S^{2-} are ions in solution in water.

The concentration of sulfide ions in such a solution can be raised or lowered by decreasing or increasing the concentration of the hydronium ions. This is an application of Le Chatelier's Principle.

The solubility of metallic sulfides varies greatly. Copper sulfide, CuS , mercury(II) sulfide, HgS , bismuth sulfide, BiS , and antimony sulfide, SbS , precipitate even in concentrated acid solutions when the concentration of sulfide ions is very small. But zinc sulfide, ZnS , manganese(II) sulfide, MnS , cobalt(II) sulfide, CoS , and nickel(II) sulfide, NiS , precipitate only in basic solutions when the concentration of S^{2-} ions is much higher. This means that the pH of the solution must be carefully controlled if we are to get a positive test for these ions. How can this be done? Buffers are useful in regulating the pH because they are solutions of a weak acid or a weak base with a salt of the acid or base. When either hydronium ions or hydroxide ions are added to the solutions, the equilibrium shifts to decrease the excess ion, thus maintaining a fairly constant pH.

We will use ammonia water with the salt ammonium chloride, NH_4Cl , dissolved in it as a buffer solution to maintain sufficient basicity to precipitate the sulfides of zinc, manganese, cobalt and nickel:



The presence of ammonium ions from the ammonium chloride helps to control the concentration of hydroxide ions, thus permitting the precipitation of the sulfides of zinc, manganese, cobalt, and nickel. The use of a buffer keeps the pH in the desired range.

Hydrolysis and Ionic Theory

When certain salts dissolve in water, the solution becomes basic or acidic. This is called hydrolysis, as you learned in Chapter 4. As a result, ions from certain salts can be used in buffer solutions as common ions with a weak acid or a weak base. The use of ammonium chloride described above is an example. Ionic salts dissociate in water to release positive and negative ions because the attractive action of water dipoles overcomes the electrostatic attraction tending to hold the ions in the solid state. Therefore, types of bonding, the nature of the solution mechanism, and degree of solubility are all involved in our understanding of the procedure used in qualitative analysis.

Spectroscopic Properties of Cations

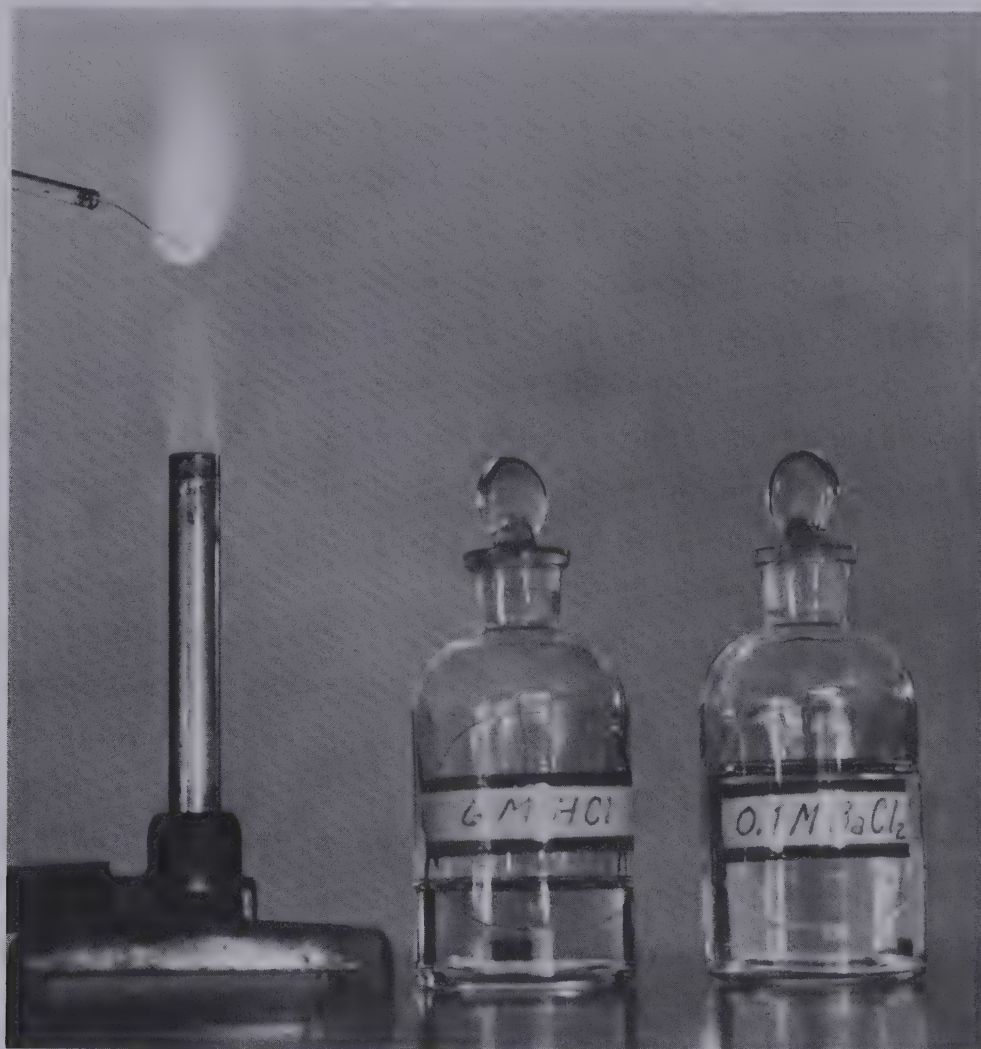
In Exp. 5-2 you observed the characteristic colors which certain metallic ions impart to the Bunsen flame. We will use these colors as confirmatory tests for copper, barium, strontium, sodium, and potassium ions. Other confirming tests are also used for the identification of these metals, but the flame test is one of the most important. It is a very specific test as only the presence of a particular ion will result in the flame color associated with it.



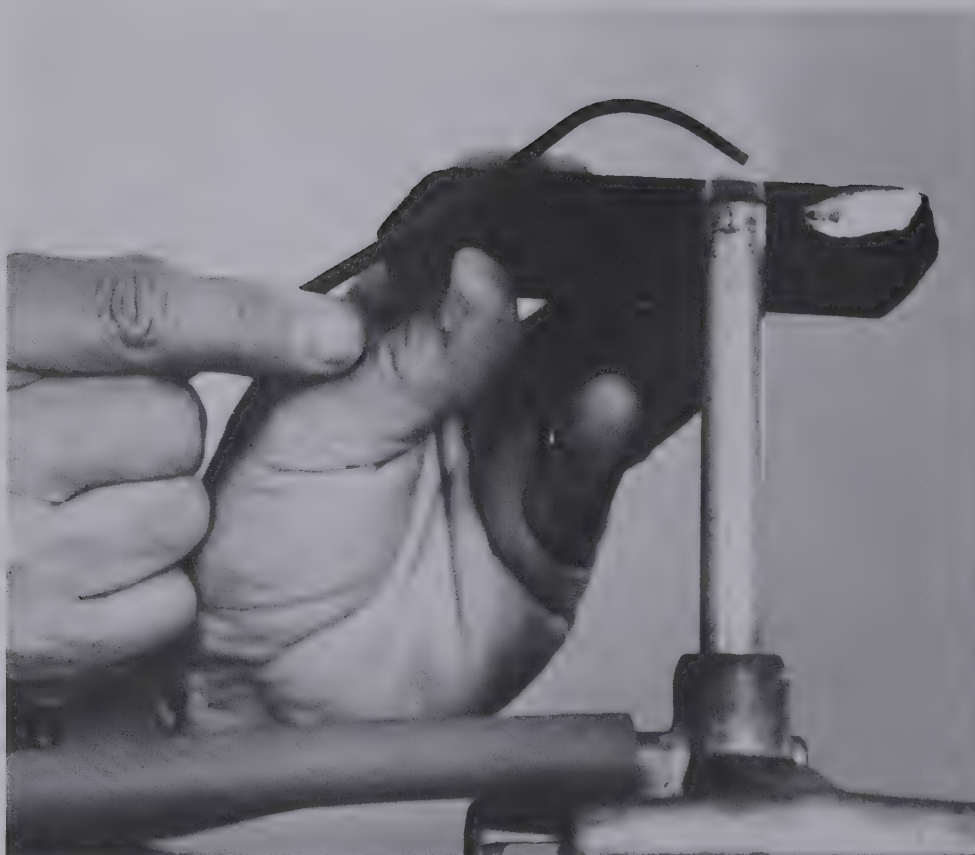
The flame test for metallic ions.

A compound known as borax, with the chemical name of sodium tetraborate, $\text{Na}_2\text{B}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, may be used to form a clear, glass-like bead to which certain metallic ions impart a characteristic color. If a platinum wire with a loop on the end is dipped into powdered borax and held in a flame, the borax swells, loses its water of hydration, and fuses into a clear bead. The bead is cooled, dipped into the unknown solution, and then heated strongly in an oxidizing flame. The metallic oxide formed reacts with the borax to impart a characteristic color to the bead. The borax bead test is helpful in identifying a few of the metals we will encounter in qualitative analysis.

The borax bead test for metallic ions.



Cobalt nitrate solution is also used for color identification of certain metals. Some of the unknown solution is placed on a charcoal block and heated strongly with the oxidizing flame of a blowpipe. This forms an oxide of the metal. A few drops of cobalt nitrate solution are then placed on the metallic oxide, and again the mixture is strongly heated with the blowpipe. The cobalt nitrate decomposes into cobalt oxide, which combines with the metallic oxide previously formed on the charcoal. Aluminum, zinc, and magnesium give characteristic colored compounds in this test. The colors of cobalt nitrate tests, borax bead tests, and flame tests are summarized in Table 11-1.



The cobalt nitrate test for metallic ions.

Characteristic Colors Displayed by Metals in
Flame, Cobalt Nitrate, and Borax Bead Tests.

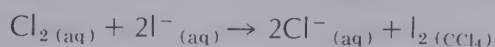
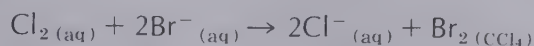
Metal	Flame Color	Cobalt Nitrate Color	Borax Bead Color
copper	bright green		
barium	yellowish-green		
strontium	bright red		
sodium	yellow (persistent)		
potassium	violet		
zinc		green	
aluminum		blue	
magnesium		pink	
chromium			green
cobalt			deep blue
nickel			brown
manganese			pink-violet

Table 11-1

Nonmetal-Ion Reactions

When a solution of chlorine in water is added to a water solution containing bromide ions, a reaction takes place. Chloride ions and bromine molecules, Br_2 , are formed. These molecules of bromine dissolve readily in carbon tetrachloride, producing an orange colored solution. Chlorine in water solu-

tion also reacts with iodide ions to form chloride ions and iodine molecules, I_2 , which dissolve in carbon tetrachloride to give a violet colored solution.



Note that the molecular forms, Br_2 and I_2 , rather than the ionic forms, Br^- and I^- , dissolve in carbon tetrachloride to give the colored solutions. These reactions can be used as tests to determine which halogen is present in an unknown solution. Look at the color photo at the top of page 122 for the appearance of positive tests.

11-2. RECORD KEEPING

In qualitative analysis, a careful record of reagents used, results observed, difficulties encountered, and conflicting evidence is vital to successful identification of unknowns and to effective communication of results. Your notebook should be permanently bound; no pages should be removed and no entry deleted. The date of your work, the code number of the unknown, and the procedure followed for each group test and all confirmatory tests are important. Chemical equations representing the positive tests should be written correctly, and the precipitate should be underlined and its color noted. In the procedure you will be using, it is important that your conclusions be based upon *all* available evidence and *not* upon any single test. If it becomes necessary to alter data, do so by drawing a line through the incorrect record, but leave it legible in case you need to refer to it later.

Intellectual integrity is the mark of a science student as well as a scientist. Your records must be as honest as possible. Personal interpretation and bias should be kept to a minimum. Your notebook is good if another person skilled in chemistry can take it, read it and, by following the procedures indicated, duplicate your work and arrive at the same conclusions.

11-3. IMPORTANT PRECAUTIONS

Most of the errors made in qualitative analysis are caused by carelessness. Therefore, your attention is called to some of the common sources of error.

Using Too Much Reagent

Many students feel that if a little reagent is useful, a large quantity is even better. This belief can be fatal to good results. Too much of a reagent may cause a precipitate to dissolve again. One example is in the use of hydrochloric acid to precipitate the Group I metallic ions (Ag^+ , Hg_2^{2+} , Pb^{2+}). Addition of too much of a certain reagent may also interfere with tests which follow. Another pitfall in using more of a reagent than is needed is that you may dilute the unknown to a point where positive identification of the ions is impossible.

Using Too Little Reagent

If there is a marked difference between the solubilities of two precipitates being formed, adding too little of the precipitating reagent may cause the

more insoluble one to be completely precipitated while the other may not be precipitated at all. In testing for the Group I metallic ions, adding too little hydrochloric acid may precipitate silver chloride but not the lead chloride. One test which may help you to determine whether sufficient reagent has been added is to permit the precipitate to settle and then add one or two more drops of the precipitating reagent. If additional precipitate forms, you have not added enough of the reagent.

Using An Impure Reagent

Every precaution is taken by your teacher to provide pure reagents. It is part of your responsibility to keep them pure. Stirring rods and pipettes should never be inserted into reagent bottles. If you need only a small quantity, pour one or two cc's of the reagent into a small, clean test tube and pipette from that. Pour the unused reagent into the sink. Solutions of sodium carbonate, Na_2CO_3 , and the strong bases may dissolve tiny amounts of glass from their containers. If such solutions appear cloudy or acquire flakes in them, call them to the attention of your teacher so they can be replaced. Sodium, calcium, and silica compounds may be contaminants from this glass; these can give misleading test results.

Improper Washing of Precipitates

Precipitates may absorb soluble substances which can interfere with tests. Careful washing with distilled water removes these impurities. Remember that the filter paper itself needs washing because the filtered liquid has been in contact with the paper. Some precipitates may consist of very tiny colloidal particles which will pass through the filter paper. Heating prior to filtering coagulates these colloidal particles and permits them to be caught by the filter paper. The laboratory directions will tell you when this should be done.

Failure to Label Tests

Label all filtrates and precipitates which are to be used in later tests. If you store these for use during a subsequent laboratory period, be sure to indicate what part of the procedure has been done so you will begin at the proper point in your testing. Of course, the labels need to be removed when they no longer apply.

11-4. REPORTING RESULTS

After you have identified your metallic ions, your instructor will verify your results before you begin analysis on the nonmetallic ions. This is important, because in most cases you will remove the metallic ions and discard them prior to testing for the nonmetallic ions. If you have made an error in your identification, it is good to know it before discarding your solutions. Also, knowledge of the metallic ions present can provide valuable clues to the possible presence of certain anions. For instance, if one of the cations is lead, you could rule out the presence of the sulfate ion since your original unknown

was in solution. Knowing that lead sulfate is relatively insoluble in water would save you time in not testing for the sulfate ion.

When you ask your teacher for verification of your results, be ready to tell him what you think you have, how you tested for the ions, what the precipitates are called, and how you reached your conclusions. Do not wait for him to ask you for this information. He will probably ask you to tell the function of the various reagents. Try to understand the nature of the observed reactions as fully as possible. After all, that is the major purpose of this unit.

11-5. REVIEW AND PREVIEW

You have completed a general survey of the field of inorganic chemistry. We have tried to present various ways in which these principles and concepts are important in your daily living and to open up some of the exciting areas of research in modern chemistry. Whether you continue your study of science or not, perhaps you will have a greater understanding of chemistry and an appreciation for its place in our lives. If you do pursue the study of science, you will have a foundation upon which to build.

Suggestions for Creative Work

1. Devise a procedure for separating cations which are in two different groups.
2. Devise a procedure for separating anions which are in more than one group.
3. Determine the pH range in which Group II cations will precipitate.
4. Determine the pH range in which Group IV cations will precipitate.

Suggestions for Creative Writing

1. Write a paper in which you discuss a minimum of three major concepts which serve as connecting themes in the study of elementary chemistry. State the concepts and cite illustrations to show how they serve to coordinate the interpretation of isolated observations.

Practice Exercises *(Answers on p. 324)*

1. Complete and balance the following equations:
 - a. $\text{Cl}_2 + \text{NaI} \rightarrow$
 - b. $\text{H}_2\text{S} + \text{HgCl}_2 \rightarrow$
 - c. $\text{NH}_4\text{OH} + \text{Al}_2(\text{SO}_4)_3 \rightarrow$
 - d. $(\text{NH}_4)_2\text{S} + \text{Ni}(\text{NO}_3)_2 \rightarrow$
2. Identify the following cations:
 - a. Gives a white precipitate with HCl; soluble in hot water; gives yellow precipitate with K_2CrO_4 .
 - b. Gives a red-brown precipitate with NH_4OH in the presence of NH_4Cl ; gives a deep blue precipitate with $\text{K}_4\text{Fe}(\text{CN})_6$.
3. Identify the following anions:
 - a. Gives a yellowish precipitate with AgNO_3 ; gives a violet colored layer in CCl_4 upon the addition of Cl_2 water.
 - b. Causes effervescence in presence of HCl; gives a gray precipitate with AgNO_3 .

4. Cite the characteristic flame colors for the following cations: (a) barium, Ba^{2+} ; (b) potassium, K^+ ; (c) strontium, Sr^{2+} ; (d) sodium, Na^+ .
5. Cite the characteristic cobalt nitrate test colors for the following cations: (a) zinc, Zn^{2+} ; (b) magnesium, Mg^{2+} ; (c) aluminum, Al^{3+} .
6. Cite the characteristic borax bead colors for the following cations: (a) nickel, Ni^{2+} ; (b) cobalt, Co^{2+} ; (c) chromium, Cr^{3+} .
7. Explain the function of Cl_2 water and CCl_4 in the bromide-iodide test.
8. Explain the function of NH_4Cl in the Group III cation test.
9. Explain the function of Na_2CO_3 in preparing a solution for anion tests.
10. Why must cations in Groups I through V be removed before testing for anions?
11. State Le Chatelier's Principle and cite one example of its application in qualitative analysis.
12. Cite one example to illustrate the importance of controlling the pH of solutions when testing for cations.
13. (Assertion-Reason; see special directions in Appendix 13)

ASSERTION

REASON

Solutions must be slightly basic when testing for Group II cations

Because their compounds are soluble in acidic solutions.

Self-Test *(Answers on pp. 324, 325)*

1. Complete and balance the following equations:
 - a. $\text{Na}_2\text{CO}_3 + \text{CoCl}_2 \rightarrow$
 - b. $\text{H}_2\text{S} + \text{CuSO}_4 \rightarrow$
 - c. $(\text{NH}_4)_2\text{S} + \text{Mn}(\text{NO}_3)_2 \rightarrow$
 - d. $\text{K}_2\text{CrO}_4 + \text{Na}_2\text{SO}_4 \rightarrow$
2. Identify the following cations:
 - a. Gives a black precipitate with $(\text{NH}_4)_2\text{S}$ in the presence of NH_4Cl ; gives a blue borax bead.
 - b. Gives a white gelatinous precipitate with ammonia water in the presence of NH_4Cl ; gives a blue cobalt nitrate test.
3. Identify the following anions:
 - a. Gives a white precipitate with BaCl_2 which is insoluble in HCl .
 - b. Gives a brown ring in the presence of freshly prepared FeSO_4 and concentrated H_2SO_4 .
4. Cite the characteristic flame colors for the following cations: (a) strontium, (b) sodium, (c) copper, (d) potassium.
5. Cite the characteristic cobalt nitrate test colors for the following cations: (a) zinc, (b) aluminum.
6. Cite the characteristic borax bead colors for the following cations: (a) chromium, (b) cobalt, (c) nickel.
7. Explain the function of Cl_2 water in the iodide test.
8. Explain the function of HCl in the Group II cation test.
9. Explain the function of NH_4Cl in the Group IV cation test.
10. Explain the function of AgNO_3 in the Group III anion test.
11. State Le Chatelier's Principle and cite one example of its application in qualitative analysis.
12. (Multiple Completion; see special directions in Appendix 13)
Sodium carbonate, Na_2CO_3 , is added to the "unknown" before testing for

most anions in order to

1. increase the pH of the solution
2. precipitate the cation
3. decrease the pH of the solution
4. keep the anion in solution

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APPENDICES 1. THE METRIC SYSTEM OF MEASUREMENT

A. STANDARD UNITS OF MEASURE

Quantity	Unit	Abbreviation
Mass	gram	g
Length	meter	m
Volume	liter	l

B. PREFIXES

These are used with the standard units of metric measure (gram, meter, and liter).

Prefix	Abbreviation	Value
kilo-	k	$1000 \times \text{unit}$
hecto-	h	$100 \times \text{unit}$
deca-	dk	$10 \times \text{unit}$
deci-	d	$0.1 \times \text{unit}$
centi-	c	$0.01 \times \text{unit}$
milli-	m	$0.001 \times \text{unit}$

Examples: cg = centigram = 0.01 gram
km = kilometer = 1000 meters

C. OTHER METRIC UNITS OF LENGTH

Unit	Abbreviation	Value
micron	μ	10^{-4} cm
millimicron	m μ	10^{-7} cm
angstrom	\AA	10^{-8} cm

D. EQUIVALENTS

1 cubic centimeter (cc)	= 1 ml
1 inch	= 2.54 cm
1 quart	= 0.95 l
1 pound	= 454 g
1 ounce	= 28.25 g

2 • EXPONENTIAL NOTATION, POWERS OF TEN

The use of very large or very small numbers in chemistry makes knowledge of powers of ten very convenient. This system is sometimes called scientific notation, or exponential notation.

$10^6 = 1,000,000$	$10^{-6} = 0.000001$
$10^5 = 100,000$	$10^{-5} = 0.00001$
$10^4 = 10,000$	$10^{-4} = 0.0001$
$10^3 = 1,000$	$10^{-3} = 0.001$
$10^2 = 100$	$10^{-2} = 0.01$
$10^1 = 10$	$10^{-1} = 0.1$
$10^0 = 1$	$10^0 = 1$

In the expression 10^3 , the *base* is 10 and the *exponent* is 3.

RULES FOR USING EXPONENTS

1. In multiplication: exponents of like bases are *added*.

Example: $10^4 \times 10^7 = 10^{11}$

$$10^{-2} \times 10^3 = 10^1$$

2. In division: exponents of like bases are *subtracted*.

Examples: $\frac{8 \times 10^2}{2 \times 10^{-6}} = 4 \times 10^8$

$$\frac{10^4}{10^5} = 10^{-1}$$

3. SIGNIFICANT FIGURES

In scientific work all the figures in a number have meaning or significance. For example, to write "2 eggs" as part of a recipe is satisfactory, but to specify exactly two grams, we would write "2.000 grams," or even more precisely, "2.0000000 grams."

Everyone knows that "2 eggs" means two eggs, no more, no less. But "2 grams" does not convey very much information. When we write "2.0 grams" we mean two and zero tenths grams. If we write "2.000 grams" we mean two and zero tenths, zero hundredths, and zero thousandths grams. The zeroes are significant—they have meaning.

The reason for this kind of scientific fussiness is that we can measure pretty finely in the laboratory, and in order for one scientist to speak to another clearly, both must follow the same rules in their use of numbers.

For example, if you are told to find the weight of a spoonful of sugar, you should report the weight to the best of your ability using the weighing device available to you in the laboratory. Suppose you had a balance which could weigh to a hundredth of a gram. Then, you should report the weight to the nearest hundredth of a gram: "6.75 grams" or whatever the weight might be. This would mean that the weight was six grams plus seven tenths of a gram plus five hundredths of a gram, as nearly as you could tell. You would be saying that you are sure of the six grams and sure of the seven tenths of a gram, and more or less sure of the five hundredths of a gram.

In using significant figures correctly, it is always understood that the last figure on the right might be off a little bit, but all the other figures are right (as far as a person can tell by doing careful work).

Suppose that you had a grandmother who was very old, 105 years old maybe. In the 105 number there are three significant figures, the 1, the 0, and the 5. Since we are not sure of her birthday, let us suppose she actually might be closer to 106 than 105, and we have followed the rules: the last figure on the right can be off a little, if it is our best guess, but the others ought to be on the button. In talking with friends, you might say, "My grandmother is about one hundred years old." But, scientifically, we could not write that she was 100 years old, since the last figure, the second 0, is off by more than a little bit; it is not a guess; it is not the best we can do, scientifically speaking.

Suppose next that we think of a lightweight person, say a pupil in the third grade who weighs 50.38 pounds. The 5, the 0, the 3, and the 8 are all significant, let us suppose, because we watched the scales when this child was weighed. What is the weight in tons? To find out, divide 50.38 pounds by 2000 pounds per ton. The answer is 0.02519 tons.

As we know, the first 0, before the decimal point, and the next zero, after the decimal point, came from the arithmetic. These two zeros tell us only where the decimal point is. In numbers like this, we *always* put one zero before the decimal point, as a good scientific number habit. The other zero then further places the decimal point. Only the 2, 5, 1, and 9 are significant figures because they tell us how much. Remember, the two zeros tell us only where the decimal point is.

Now we can summarize the rules for determining significant figures:

1. All non-zero digits *are* significant. Each of these numbers contains three significant figures: 425, 25.2, 1.61, 19.5
2. All zeroes between non-zero digits *are* significant. The zeroes in each of these *are* significant: 590.5, 15.03, 3.08, 27.0005
3. Final zeroes to the left of a decimal point *are* significant. These zeroes *are* significant: 315,000.; 250.; 60.
4. Final zeroes to the left of an understood decimal point *are not* significant. The following numbers each have three significant figures: 315,000; 1,050,000; 2060
5. Final zeroes to the right of a decimal point *are always* significant. These numbers have three significant figures: 0.390, 45.0, 20.0, 0.800.
6. Zeroes at the beginning of a number *are not* significant. They simply mark the place for the decimal point. *None* of these zeroes is significant; each number contains only three significant figures: 0.00574, 0.0376, 0.826

Problems: Determine the number of significant figures in each of the following:

- | | |
|-----------|-----------|
| 1. 87.1 | 5. 0.04 |
| 2. 26.0 | 6. 3.002 |
| 3. 0.0001 | 7. 6400.8 |
| 4. 47,000 | 8. 52,000 |

ADDITION AND SUBTRACTION OF NUMBERS

The rules for addition and subtraction are easy and are based on common sense. For example, add these numbers:

$$\begin{array}{r} 6.3 \text{ cm} \\ 10.794 \text{ cm} \\ \underline{4.81 \text{ cm}} \end{array}$$

Common sense tells us that we cannot yet add these numbers. That is, from the basis of significant figures and their use, in the "6.3" we are sure of the "6" and pretty sure of the ".3" but we do not know anything about the hundredths or thousandths places. For the "4.81" we know nothing about the thousandths place. So, this is what we are trying to add:

$$\begin{array}{r} 6.3?? \text{ cm} \\ 10.794 \text{ cm} \\ \underline{4.81? \text{ cm}} \end{array}$$

If we try to add this, the first question might be: What is the sum of ? + 4 + ?, in the thousandths place? No one knows the answer to this one.

The same difficulty comes up again when we try to add in the hundredths column, because no one knows what the sum of 1 + 9 + ? is, either.

Now, with this in mind, let us add as best we can:

$$\begin{array}{r} 6.3?? \text{ cm} \\ 10.794 \text{ cm} \\ \underline{4.81? \text{ cm}} \\ 21.904 \text{ cm} \\ ?? \end{array}$$

A question mark is put under the zero and the four to indicate that we are not at all sure of their validity. Since we are not very sure about these, in the final sum, they should be dropped. The correct sum, by the rules for significant figures is 21.9 cm.

Let us try this again with a different set of numbers to add:

$$\begin{array}{r} 5.8?? \text{ cm} \\ 16.579 \text{ cm} \\ \underline{4.81? \text{ cm}} \\ 27.189 \text{ cm} \\ ?? \end{array}$$

As you know, we should drop the 8 and the 9 since we are not very sure about them. However, we could say that we have some small idea that they are not entirely wrong. The real sum is probably closer to 27.2 cm than it is to 27.1 cm.

Whenever the dropped digit just to the right of the last digit to be kept is 5 or more, we increase the last digit we are keeping by 1. So, if the trial sum is 27.189 cm, the 8 is bigger than 5, and we increase the 1 to make it 2. This is called *rounding off*.

Suppose we had this for a trial sum:

$$\begin{array}{r} 63.6 \text{ liters} \\ ? \end{array}$$

The final 6 is larger than 5, so when it is dropped, the 3 is changed to a 4. The correct answer is 64 liters, in this case.

The rules for addition are:

1. List the numbers to be added, and fill in empty columns with question marks.
2. Add the numbers in the usual way, but put a question mark under any digit in the sum that has a question mark in the column above it.
3. Drop the digits with question marks under them in the sum, rounding off if necessary. The rule for rounding off is that if the dropped digit just to the right of the last digit kept is less than 5, do not change the number. If it is 5 or more, increase the last digit kept by 1.

Subtraction rules are the same as those for addition. Briefly, use the question marks, drop digits, and round off according to the same rounding off rules. Try this one:

$$\begin{array}{r} 67.874 \text{ grams} \\ -12.34? \text{ grams} \\ \hline 55.534 \text{ grams} \\ ? \end{array}$$

When we drop the 4 with the question mark under it, we notice that it is less than 5, so the last digit now on the right, the 3, is not changed; the correct answer is 55.53 grams.

Problems:

Give the answers to the correct number of significant figures in each case, rounding off where necessary.

- | | | | | | |
|----|---------------|----|-------------|----|-----------------|
| 1. | 1.28 | 3. | 0.001 | 5. | 6400 |
| | 0.49 | | 0.082 | | 375 |
| | <u>0.062</u> | | <u>0.03</u> | | <u>25950</u> |
| 2. | 95.3 | 4. | 3.006 | | 43.43 |
| | <u>- 6.15</u> | | <u>-1.4</u> | | <u>- 0.0029</u> |

MULTIPLICATION AND DIVISION OF NUMBERS

The rules for multiplication and division are different from those for addition and subtraction. For multiplying and dividing, follow these rules:

- Count the number of significant figures in both numbers to be multiplied or divided. The number resulting from the multiplication or division cannot have more significant figures than the least number of significant figures in either of the two original numbers.

Suppose you are to multiply 1.230 by 6.7, for example. One number has four significant figures, the other has two significant figures. Their product, therefore, should have two significant figures.

Or suppose you are going to divide 1.23 by 45.6; then since both numbers have three significant figures, the answer should also have three significant figures.

- Multiply or divide in the ordinary way. But if you do not wish to, you need not carry out the answer to all the extra digits. You must carry only one more digit than the final number of significant figures.

For example, let us divide 36.453 grams by 22.4 liters.

$$\frac{36.453 \text{ grams}}{22.4 \text{ liters}} = 1.627 \text{ grams/liter}$$

We need not go further in the division, to 1.62736, for example. We can stop dividing as soon as we have one more digit than three digits, the number of significant figures in the 22.4 liters.

- Finally, round off the answer to the correct number of significant figures.

To use our example further, the result of our division has four digits, 1.627, so we now round this off to three significant figures by dropping the 7, as though it had a question mark under it. Dropping the 7 requires that we change the 2 that is now on the right to a 3. The correct answer is 1.63 grams/liter.

For multiplication we use the same rules. Try 56.7 times 4.3210. When we multiply this out all the way, we get 245.00070 as the product. But this is not the accepted correct answer according to the rules for significant figures. There should be three significant figures in our answer, so we drop the other digits, as though they had question marks under them, and obtain 245.

Problems:

1. Multiply the following numbers and express the product to the correct number of significant figures:
 - a. $3.72 \times 2.1 =$
 - b. $0.0145 \times 0.0089 =$
 - c. $12.9 \times 1.23 =$
2. Divide the following numbers and express the quotient to the correct number of significant figures.
 - a. $4.58 \div 6.600 =$
 - b. $71.8 \div 0.99 =$
 - c. $9.08 \div 21.4 =$

4. NAMING COMPOUNDS

The rules for naming compounds are somewhat variable and it is difficult to cover all cases by stating simple guidelines. The rules given below will serve for most of your work in beginning chemistry.

A. BINARY COMPOUNDS (Those containing only two elements)

1. Place the name of the element with positive oxidation number first.
2. The element with negative oxidation number is named by adding the suffix *-ide* to the stem. Example: NaCl = sodium chloride. *Chlor-* is the stem of chlorine.

B. PSEUDO-BINARY COMPOUNDS (Those composed of a metallic ion and a polyatomic ion)

1. Place the name of the metallic (positive) ion first.
2. Follow this with the name of the polyatomic ion. Example: Na_2CrO_4 = sodium chromate. CrO_4^{2-} is a polyatomic ion known as chromate.

C. NAMING BASES

1. All bases contain the hydroxide (OH^-) ion as the negative ion. This is in combination with a metallic ion; therefore, the rules for naming pseudo-binary compounds apply. Example: KOH = potassium hydroxide.

D. NAMING ACIDS

Binary Acids

1. Determine what element is in combination with hydrogen.
2. To the stem of this element, add the prefix *hydro-* and the suffix *-ic*. Example: HCl = hydro-chlor-ic acid (hydrochloric acid).

Ternary Acids (Those containing three elements)

Most of the common acids contain hydrogen, oxygen, and one other non-metallic element. These are known as *oxyacids*. Since these are the ones with which we are mainly concerned, the rules below apply to oxyacids.

1. Determine the proper stem by noting what element is present in addition to hydrogen and oxygen.
2. If more than one acid is formed from the same three elements:
 - a. to name the most common one of the group, add the suffix *-ic* to the stem and use no prefix. Examples: sulfuric, H_2SO_4 ; nitric, HNO_3 ; chloric, HClO_3
 - b. the acid in the series having *less* oxygen than the most common one is named by adding the suffix *-ous* to the stem. Examples: sulfurous, H_2SO_3 ; nitrous, HNO_2 ; chlorous, HClO_2 .
 - c. if a third acid in the series has still less oxygen, it is named by using the prefix *hypo-* and the suffix *-ous*. Example: hypochlorous, HClO
 - d. if an acid contains more oxygen than the most common member of the series, it is named by using the prefix *per-* and the suffix *-ic*. Example: perchloric, HClO_4

The only way to know whether there are one or several acids composed of the same three elements is by experimentation. Otherwise, you will be told which member of a group is the common one.

Summary, Oxyacids					
Name of acid	Formula	Number of oxygen atoms	Prefix	Stem	Suffix
sulfuric	H_2SO_4	4	_____	sulfur-	-ic
sulfurous	H_2SO_3	3	_____	sulfur-	-ous
perchloric	HClO_4	4	per-	chlor-	-ic
chloric	HClO_3	3	_____	chlor-	-ic
chlorous	HClO_2	2	_____	chlor-	-ous
hypochlorous	HClO	1	hypo-	chlor-	-ous

5 · FORMULA WRITING

DEFINITIONS

Symbol A letter or letters which stand for (1) an element, (2) one atom of that element, and (3) one mole of the atoms of the element.

Formula (1) A group of symbols which represents the ratio in which atoms combine to form a compound; (2) a symbol or group of symbols which represents one mole of molecules or ions.

Ion An atom or group of atoms possessing an electric charge.

Subscript An integer written at the lower right of a symbol or parenthesis in a formula to indicate the number of moles of atoms or ions contained in one mole of the substance.

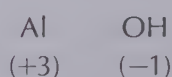
Oxidation number A small number, positive or negative, which is assigned to an element or ion and which is useful when writing formulas for compounds and ions. The sum of all the oxidation numbers equals zero for all compounds and equals the charge for ions.

RULES

1. Write the symbol for the element or ion with the positive oxidation number first.
2. Follow this with the symbol of the element or ion with the negative oxidation number.
3. Use subscripts to make the sum of the oxidation numbers equal zero for compounds or equal the charge for ions.
4. When a subscript is used with an ion containing two or more elements, the ion **MUST** be enclosed in parentheses **BEFORE** writing the subscript.

Sample problem Write the correct formula for the compound aluminum hydroxide.

Solution Write the symbols aluminum and hydroxide but *omit* the charges for the ions. Instead, write the oxidation numbers in parentheses below the symbols.



Notice that the oxidation numbers do not add up to zero. We need three hydroxide ions to get an oxidation number of -3 that will cancel the $+3$ for aluminum. We put the hydroxide symbol in parentheses and add the subscript 3 to indicate the 3 hydroxide ions.



Note: The following elements exist in diatomic molecules and their correct molecular formulas are given:



Whenever these elements occur in an *uncombined* state, they **MUST** be represented as indicated above. Not observing this rule is one of the commonest errors made by students learning to write formulas and equations.

6. CHARGES AND OXIDATION NUMBERS OF COMMON IONS

Oxidation Number	Name of Ion	Formula	Oxidation Number	Name of Ion	Formula
+1	ammonium	NH_4^+	-1	acetate	$\text{C}_2\text{H}_3\text{O}_2^-$
	copper(I)	Cu^+		bromide	Br^-
	hydrogen	H^+		chlorate	ClO_3^-
	lithium	Li^+		chloride	Cl^-
	potassium	K^+		chlorite	ClO_2^-
	silver	Ag^+		fluoride	F^-
	sodium	Na^+		hydrogen	
				carbonate	HCO_3^-
+2				hydroxide	OH^-
				hypochlorite	ClO^-
				iodide	I^-
				nitrate	NO_3^-
				nitrite	NO_2^-
				perchlorate	ClO_4^-
				permanganate	MnO_4^-
				thiocyanate	SCN^-
			-2	carbonate	CO_3^{2-}
	barium	Ba^{2+}		chromate	CrO_4^{2-}
	calcium	Ca^{2+}		dichromate	$\text{Cr}_2\text{O}_7^{2-}$
	chromium(II)	Cr^{2+}		oxalate	$\text{C}_2\text{O}_4^{2-}$
	cobalt	Co^{2+}		sulfate	SO_4^{2-}
	copper(II)	Cu^{2+}		sulfite	SO_3^{2-}
	iron(II)	Fe^{2+}		thiosulfate	$\text{S}_2\text{O}_3^{2-}$
	lead(II)	Pb^{2+}	-3	ferricyanide	$\text{Fe}(\text{CN})_6^{3-}$
	magnesium	Mg^{2+}		phosphate	PO_4^{3-}
	manganese(II)	Mn^{2+}	+3		
	mercury(I)	Hg_2^{2+}			
	mercury(II)	Hg^{2+}			
	tin(II)	Sn^{2+}			
	zinc	Zn^{2+}	+4		
+3	aluminum	Al^{3+}			
	antimony(III)	Sb^{3+}			
	chromium(III)	Cr^{3+}			
	iron(III)	Fe^{3+}			
+4	tin(IV)	Sn^{4+}	-4	ferrocyanide	$\text{Fe}(\text{CN})_6^{4-}$

7. EQUATION WRITING

DEFINITIONS

Coefficient An integer written at the left of a formula which indicates the number of moles we are dealing with.

Reactant A substance with which you *begin* in performing an experiment; always written on the *left side* of a chemical equation.

Product A substance *produced* by a chemical reaction; always written on the *right side* of a chemical equation.

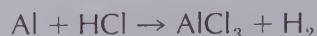
RULES

1. Remember, we do not consider an equation correct unless it represents accurately what takes place in the laboratory.
2. Determine the reactants and the products in the reaction and the correct formulas for all reactants and products. This step is of *utmost* importance, because if a formula is written incorrectly it may be impossible to balance the equation.
3. Write the chemical sentence, showing the reactants on the left side of the arrow and the products on the right side.
4. Balance the equation. This means there must be the same number of moles of atoms of each element on both sides of the equation. Matter is conserved in all chemical reactions and our equation must indicate that this is so.
 - a. We balance many equations by inspection. That is, we simply look at the formulas, count the number of atoms of each element on each side of the equation, and write the proper *coefficients* to make them equal.
 - b. NEVER change a subscript in balancing an equation! This alters the formula and you must use correct formulas in the equation.
 - c. Keep coefficients as small as possible in most cases. If you plan to try different coefficients, begin with the integer 2 and work up as necessary. In most cases it is desirable that a balanced chemical equation indicate the *least* number of moles.

Sample Problem One of the first reactions you observed was that between aluminum and hydrochloric acid to produce aluminum chloride and hydrogen gas. Write the balanced equation for the reaction.

Solution English sentence: Aluminum reacts with hydrochloric acid to yield aluminum chloride and hydrogen.

Chemical sentence:

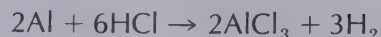


Balancing: By inspection, we find one mole of chlorine atoms on the left side and 3 moles of chlorine atoms on the right side of the equation. We can place the coefficient 3 in front of HCl, giving 3 moles of chlorine atoms on the left.



But one mole of hydrogen molecules contains 2 moles of hydrogen atoms. The lowest common multiple of 2 and 3 is 6. Therefore, if we use 6 moles of

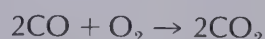
HCl, we get 3 moles of hydrogen molecules. Six moles of HCl will produce 2 moles of AlCl_3 . We will then need 2 moles of Al atoms. This gives us a chemical equation, complete and balanced.



Sometimes you may have to erase coefficients as you proceed with inspection of the equation. This is to be expected. Just work your way through the process one step at a time. Do not worry about speed; this will come with practice.

SUMMARY OF EXPERIMENTAL INFORMATION IN A CHEMICAL EQUATION

To illustrate the importance and usefulness of chemical equations, let us consider the equation for the burning of carbon monoxide. The chemical equation is:



Qualitative information:

Carbon monoxide reacts with oxygen to yield carbon dioxide.

Quantitative information:

- Two moles of carbon monoxide react with one mole of oxygen molecules to yield two moles of carbon dioxide.
- Using the weights of those moles, we get: 56 grams of carbon monoxide reacts with 32 grams of oxygen to yield 88 grams of carbon dioxide.
- Since all three are gases, and at standard conditions one mole of molecules of any gas occupies 22.4 liters, we can say further: 44.8 liters of carbon monoxide reacts with 22.4 liters of oxygen to yield 44.8 liters of carbon dioxide.

8 · COLLECTING GASES OVER WATER

When a gas is collected over water, a correction must be made for the amount of water vapor which is mixed with the gas. This is done by subtracting the pressure of the water vapor from the total pressure of the mixture. The total pressure is usually the barometric pressure. The pressure of the water vapor is called the vapor pressure of water; it is dependent upon temperature, and a table is included in this appendix for your convenience.

Partial Pressure: The partial pressure of a component of a gas mixture is the pressure which that component would exert if it alone occupied the entire volume.

Dalton’s Law of Partial Pressures: The total pressure of a gaseous mixture is equal to the sum of the partial pressures of the components.

Vapor Pressure of Water, in Torr, at Various Temperatures	
Temperature, °C	Vapor Pressure, Torr (to the nearest whole number)
0	4
5	7
10	9
15	13
17	14
18	15
19	16
20	18
21	19
22	20
23	21
24	22
25	24
30	32
35	42
40	55
50	92
60	149
70	234
80	355
90	526
100	760

Sample problem: Oxygen is collected over water at a temperature of 23°C and a barometric pressure of 745 torr. What is the partial pressure of the oxygen?

Solution: The table shows that the vapor pressure at 23°C is 21 torr. Hence, the partial pressure of the oxygen is

$745 \text{ torr} - 21 \text{ torr} = 724 \text{ torr}$

9. TEMPERATURE, PRESSURE, AND VOLUME RELATIONS FOR A GAS

A. THE EFFECT OF PRESSURE ON GAS VOLUME

According to Boyle's Law, when the temperature is kept constant, the volume of a given mass of gas varies inversely with the pressure. In mathematical terms, the product of pressure \times volume remains constant:

$$V_1 P_1 = V_2 P_2$$

Sample problem: If 100 cc of a gas is collected at a pressure of 820 torr, what will be its volume at standard pressure (760 torr) if the temperature remains constant?

Solution:

1. If the pressure is decreased, the volume will increase. Therefore, the new volume must be more than 100 cc.
2. $100 \text{ cc} \times 820 \text{ torr} = \text{new volume} \times 760 \text{ torr}$
 $\text{new volume} = 108 \text{ cc}$

B. THE EFFECT OF TEMPERATURE ON GAS VOLUME

According to Charles' Law, when the pressure is kept constant, the volume of a given mass of gas varies directly with the absolute temperature:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Sample problem: If a volume of gas measures 50.0 cc at a temperature of 20°C , what will be its volume at standard temperature (0°C)?

Solution:

1. Temperatures must be converted to the Kelvin scale before solving gas problems. This is done by adding 273° to the Celsius temperature.

$$T_1 = 20^\circ\text{C} = (20 + 273)^\circ\text{K} = 293^\circ\text{K}$$

$$T_2 = 0^\circ\text{C} = (0 + 273)^\circ\text{K} = 273^\circ\text{K}$$

2. Decreasing the temperature of a gas results in a decrease in its volume. Therefore, the new volume will be less than 50.0 cc.

$$\frac{50.0 \text{ cc}}{293^\circ\text{K}} = \frac{\text{new volume}}{273^\circ\text{K}}$$

$$\text{new volume} = 46.6 \text{ cc}$$

C. THE COMBINED EFFECT OF PRESSURE AND TEMPERATURE ON GAS VOLUME

The Laws of Boyle and Charles can be combined into a general gas law when simultaneous corrections must be made for the effects of pressure and temperature on a gas volume.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Since the majority of gas calculations are concerned with determining a new volume, it is more convenient to rewrite the equation as follows.

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

In solving gas problems, try to avoid “plugging in” values. Instead, form a habit of visualizing the effect of temperature and pressure on the volume of a gas.

Sample problem: A gas is found to have a volume of 100. cc at a pressure of 740. torr and a temperature of 25°C. What volume will it occupy at standard conditions?

Solution:

1. Set up the problem data in a meaningful form, as:

$$\begin{aligned} V_1 &= 100. \text{ cc} \\ V_2 &= ? \\ P_1 &= 740. \text{ torr} \\ P_2 &= 760. \text{ torr} \\ T_1 &= 25^\circ\text{C} = (25 + 273)^\circ\text{K} = 298^\circ\text{K} \\ T_2 &= 0^\circ\text{C} = (0 + 273)^\circ\text{K} = 273^\circ\text{K} \end{aligned}$$

2. Substituting, we get

$$\begin{aligned} V_2 &= 100. \text{ cc} \times \frac{740. \text{ torr}}{760. \text{ torr}} \times \frac{273^\circ\text{K}}{298^\circ\text{K}} \\ V_2 &= 89.0 \text{ cc} \end{aligned}$$

The increase in pressure and the decrease in temperature both serve to decrease the volume.

Sample problem: A gas volume measures 100. cc when collected over water at a temperature of 23°C and a barometric pressure of 800. torr. The vapor pressure of water at 23°C is 21 torr. Calculate the volume of dry gas at STP.

Solution:

1. We set up the data as before, noting that the partial pressure of the dry gas at 23°C is the barometric pressure minus the vapor pressure of water.

$$\begin{aligned} V_1 &= 100. \text{ cc} \\ V_2 &= ? \\ P_1 &= 800. \text{ torr} - 21 \text{ torr} = 779 \text{ torr} \\ P_2 &= 760. \text{ torr} \\ T_1 &= 23^\circ\text{C} = (23 + 273)^\circ\text{K} = 296^\circ\text{K} \\ T_2 &= 0^\circ\text{C} = (0 + 273)^\circ\text{K} = 273^\circ\text{K} \end{aligned}$$

2. Substituting, we get

$$\begin{aligned} V_2 &= 100. \text{ cc} \times \frac{779 \text{ torr}}{760. \text{ torr}} \times \frac{273^\circ\text{K}}{296^\circ\text{K}} \\ V_2 &= 94.5 \text{ cc} \end{aligned}$$

10. QUANTITATIVE RELATIONS FROM EQUATIONS

A. WEIGHT-WEIGHT RELATIONS

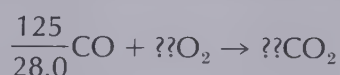
Sample problem: What is the weight of oxygen required to convert 125 grams of carbon monoxide into carbon dioxide? The molecular weight of carbon monoxide is 28.0, and the molecular weight of oxygen is 32.0.

Solution:

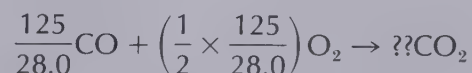
1. We write the balanced equation for the reaction.



2. Since 28.0 g of CO is one mole, the number of moles in 125 g is 125/28.0 moles. We write a new equation with 125/28.0 as a coefficient for CO (instead of 2) and unknown coefficients (question marks) for O₂ and CO₂.



3. From the balanced equation we see that half as many moles of O₂ are needed to convert a certain number of moles of CO to CO₂, so we can write



4. The last equation says that 125/28.0 moles of carbon monoxide require $\frac{1}{2} \times (125/28.0)$ moles of oxygen. Since one mole of oxygen weighs 32.0 g, the weight of that much oxygen is

$$\frac{1}{2} \times \frac{125}{28.0} \times 32.0 \text{ grams} = 71.4 \text{ grams}$$

B. WEIGHT-VOLUME RELATIONS

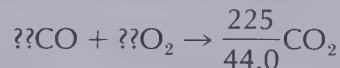
Sample problem: How many liters of oxygen would be required at standard conditions to produce 225 grams of carbon dioxide from carbon monoxide? The molecular weight of CO₂ is 44.0.

Solution:

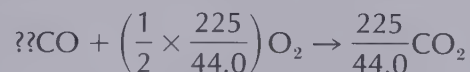
1. We write the balanced chemical equation for the reaction.



2. Since 44.0 g of CO₂ is one mole, the number of moles in 225 g is 225/44.0 moles. We write a new equation with 225/44.0 as a coefficient for CO₂ (instead of 2) and unknown coefficients (question marks) for CO and O₂.



3. From the balanced equation we see that half as many moles of O₂ molecules are needed to produce a certain number of moles of CO₂, so we can write



4. The last equation says that 225/44.0 moles of carbon dioxide are produced by using $\frac{1}{2} \times (225/44.0)$ moles of oxygen. Therefore, since one mole of

oxygen has a volume of 22.4 liters at standard conditions, the volume of that many moles is

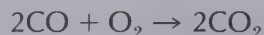
$$\frac{1}{2} \times \frac{225}{44.0} \times 22.4 \text{ liters} = 57.2 \text{ liters}$$

C. VOLUME-VOLUME RELATIONS

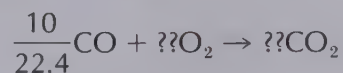
Sample problem: How many liters of oxygen would be required to convert 10 liters of carbon monoxide to carbon dioxide?

Solution:

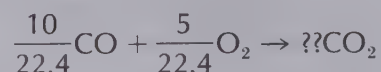
1. We write the balanced chemical equation for the reaction.



2. Since one mole of a gas takes up 22.4 liters at standard conditions, the fraction of a mole that takes up only 10 liters is $10/22.4$ mole. We write a new equation with $10/22.4$ as a coefficient for CO (instead of 2) and unknown coefficients (question marks) for O_2 and CO_2 .



3. From the balanced equation, we see that half as many moles of O_2 are required to convert a certain number of moles of CO to CO_2 , so we would need $5/22.4$ mole of oxygen molecules.



4. The last equation says that $10/22.4$ mole of carbon monoxide requires $5/22.4$ mole of oxygen molecules. Since one mole of oxygen molecules takes up 22.4 liters at standard conditions, the volume of $5/22.4$ mole is

$$\frac{5}{22.4} \times 22.4 \text{ liters} = 5 \text{ liters}$$

11 · PERCENTAGE COMPOSITION

A. DETERMINING PERCENTAGE COMPOSITION

The composition of a compound in terms of the percentage by weight of each element can be determined from its chemical formula and a table of atomic weights.

Sample problem: Determine the percentage by weight of each element in sodium carbonate, Na_2CO_3 .

Solution:

1. Find the formula weight.

$$\text{Na: } 23.0 \times 2 = 46.0$$

$$\text{C: } 12.0 \times 1 = 12.0$$

$$\text{O: } 16.0 \times 3 = \underline{48.0}$$

$$106.0$$

2. Divide the formula weight of each element in the compound by the total formula weight and multiply by 100%.

$$\text{Na: } 46.0 \div 106.0 \times 100\% = 43.4\%$$

$$\text{C: } 12.0 \div 106.0 \times 100\% = 11.3\%$$

$$\text{O: } 48.0 \div 106.0 \times 100\% = \underline{45.3\%}$$

$$100.0\%$$

Thus, sodium carbonate contains 43.4% sodium, 11.3% carbon, and 45.3% oxygen by weight.

B. DETERMINING EMPIRICAL AND MOLECULAR FORMULAS FROM PERCENTAGE COMPOSITION

Most formulas are determined by analyzing a compound in the laboratory to identify the elements present in it. After this is done, the percentage by weight of each element present is determined. The empirical formula is then calculated from this information using the weight per mole of each element.

Sample problem: A compound is known to contain 75.0% carbon and 25.0% hydrogen by weight. What is the empirical formula for the compound?

Solution:

1. Divide the % of each element by its atomic weight.

$$\text{C: } 75.0 \div 12.0 = 6.25$$

$$\text{H: } 25.0 \div 1.0 = 25$$

This gives us the relative number of atoms in the formula. The ratio of carbon atoms to hydrogen atoms is 6.25 to 25.

$$\text{C : H} = 6.25 : 25$$

2. To find the smallest ratio of atoms divide both of the above numbers by the smaller one.

$$\text{C: } 6.25 \div 6.25 = 1$$

$$\text{H: } 25 \div 6.25 = 4$$

Hence we get the empirical formula CH_4 .

We must have one additional fact if we are to know whether the empirical formula is the same as the molecular formula. The molecular weight of the substance must be determined. The molecular formula may be the same as the empirical formula or it may be some multiple of it.

Sample problem: A certain compound is composed of 80.0% carbon and 20.0% hydrogen by weight. Its molecular weight is known to be 30.0. What is the molecular formula?

Solution:

$$\text{C: } 80.0 \div 12.0 = 6.67$$

$$\text{H: } 20.0 \div 1.0 = 20$$

Divide both 6.67 and 20 by 6.67 to get the ratio of carbon atoms to hydrogen atoms, 1 to 3. Therefore, the empirical formula is CH_3 .

The empirical formula weight is

$$\text{C: } 12.0 \times 1 = 12.0$$

$$\text{H: } 1.0 \times 3 = \frac{3.0}{15.0}$$

This is one-half the molecular weight, so each subscript in the empirical formula must be multiplied by 2 for the molecular formula.

$$\text{molecular formula} = \text{C}_2\text{H}_6$$

12 • TABLE OF ATOMIC WEIGHTS

Element	Symbol	Atomic number	Atomic weight	Element	Symbol	Atomic number	Atomic weight
Actinium	Ac	89	(227)	Mercury	Hg	80	200.6
Aluminum	Al	13	27.0	Molybdenum	Mo	42	95.9
Americium	Am	95	(243)	Neodymium	Nd	60	144.2
Antimony	Sb	51	121.8	Neon	Ne	10	20.2
Argon	Ar	18	40.0	Neptunium	Np	93	(237)
Arsenic	As	33	74.9	Nickel	Ni	28	58.7
Astatine	At	85	(210)	Niobium	Nb	41	92.9
Barium	Ba	56	137.3	Nitrogen	N	7	14.0
Berkelium	Bk	97	(249)	Nobelium	No	102	(254)
Beryllium	Be	4	9.0	Osmium	Os	76	190.2
Bismuth	Bi	83	209.0	Oxygen	O	8	16.0
Boron	B	5	10.8	Palladium	Pd	46	106.4
Bromine	Br	35	79.9	Phosphorus	P	15	31.0
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.1
Calcium	Ca	20	40.1	Plutonium	Pu	94	(242)
Californium	Cf	98	(251)	Polonium	Po	84	(210)
Carbon	C	6	12.0	Potassium	K	19	39.1
Cerium	Ce	58	140.1	Praseodymium	Pr	59	140.9
Cesium	Cs	55	132.9	Promethium	Pm	61	(145)
Chlorine	Cl	17	35.5	Protactinium	Pa	91	(231)
Chromium	Cr	24	52.0	Radium	Ra	88	(226)
Cobalt	Co	27	58.9	Radon	Rn	86	(222)
Copper	Cu	29	63.5	Rhenium	Re	75	186.2
Curium	Cm	96	(247)	Rhodium	Rh	45	102.9
Dysprosium	Dy	66	162.5	Rubidium	Rb	37	85.5
Einsteinium	Es	99	(254)	Ruthenium	Ru	44	101.1
Erbium	Er	68	167.3	Samarium	Sm	62	150.4
Europium	Eu	63	152.0	Scandium	Sc	21	45.0
Fermium	Fm	100	(252)	Selenium	Se	34	79.0
Fluorine	F	9	19.0	Silicon	Si	14	28.1
Francium	Fr	87	(223)	Silver	Ag	47	107.9
Gadolinium	Gd	64	157.3	Sodium	Na	11	23.0
Gallium	Ga	31	69.7	Strontium	Sr	38	87.6
Germanium	Ge	32	72.6	Sulfur	S	16	32.1
Gold	Au	79	197.0	Tantalum	Ta	73	180.9
Hafnium	Hf	72	178.5	Technetium	Tc	43	(99)
Helium	He	2	4.0	Tellurium	Te	52	127.6
Holmium	Ho	67	164.9	Terbium	Tb	65	158.9
Hydrogen	H	1	1.0	Thallium	Tl	81	204.4
Indium	In	49	114.8	Thorium	Th	90	232.0
Iodine	I	53	126.9	Thulium	Tm	69	168.9
Iridium	Ir	77	192.2	Tin	Sn	50	118.7
Iron	Fe	26	55.8	Titanium	Ti	22	47.9
Krypton	Kr	36	83.8	Uranium	U	92	238.0
Lanthanum	La	57	138.9	Vanadium	V	23	50.9
Lawrencium	Lr	103	(256)	Wolfram	W	74	183.9
Lead	Pb	82	207.2	(Tungsten)			
Lithium	Li	3	6.9	Xenon	Xe	54	131.3
Lutetium	Lu	71	175.0	Ytterbium	Yb	70	173.0
Magnesium	Mg	12	24.3	Yttrium	Y	39	88.9
Manganese	Mn	25	54.9	Zinc	Zn	30	65.4
Mendelevium	Md	101	(256)	Zirconium	Zr	40	91.2

Note: The atomic weight for each element is based on the carbon-12 scale. Parentheses denote atomic weight for most stable or best known isotope.

13 · SPECIAL DIRECTIONS FOR PRACTICE EXERCISES AND SELF-TESTS

A. ASSERTION-REASON QUESTIONS

Each statement (assertion) in the left-hand column is followed by a reason in the right-hand column. Give answer as:

- A if both the assertion and the reason are true statements **and** the reason is a *correct explanation* of the assertion;
- B if both the assertion and the reason are true statements **but** the reason is **not** a correct explanation of the assertion;
- C if the assertion is true, but the reason is a false statement;
- D if the assertion is false, but the reason is a true statement;
- E if both assertion and reason are false statements.

Directions summarized:

- | | | | |
|---|-------|-------|--|
| A | True | True | Reason is a <i>correct explanation</i> |
| B | True | True | Reason is NOT a correct explanation |
| C | True | False | |
| D | False | True | |
| E | False | False | |

B. MULTIPLE-COMPLETION QUESTIONS

In these questions, ONE or MORE of the choices are correct. Decide which of the responses is(are) correct, then give answer as:

- A if only 1, 2, and 3 are correct;
- B if only 1 and 3 are correct;
- C if only 2 and 4 are correct;
- D if only 4 is correct;
- E if some other response (or combination of responses) of the ones given is correct.

Directions summarized:

- | | | | |
|---|--------------|---|----------------------------|
| A | 1, 2, 3 only | D | 4 only |
| B | 1, 3 only | E | some other response or |
| C | 2, 4 only | | combination of those given |

AND SELF-TESTS

PRACTICE EXERCISES (pp. 30 to 32)

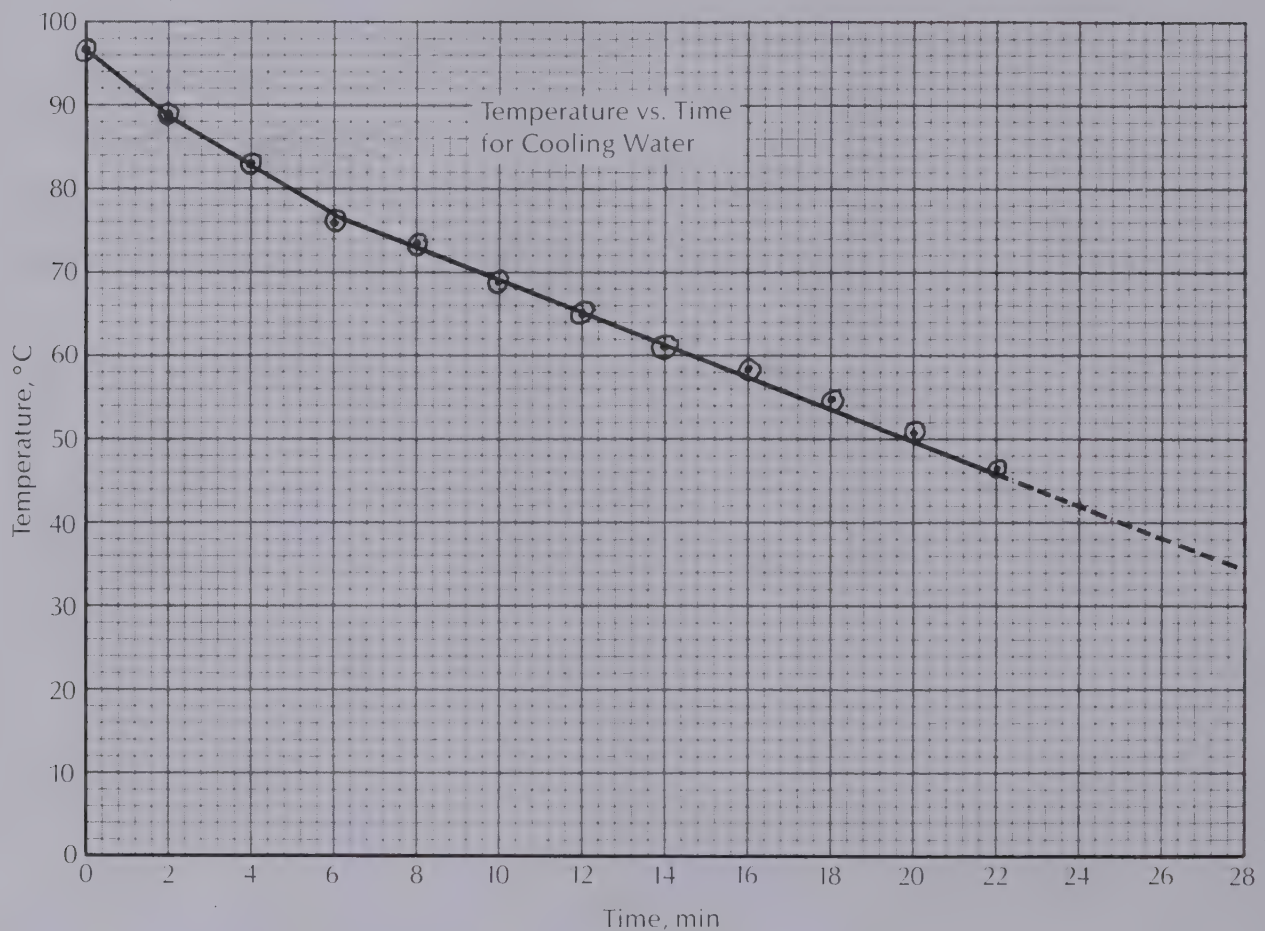
1. a. 50 mm b. 3000 cc c. 60,000 mg d. 0.025 liter e. 0.25 liter
2. a. 5 b. 2 c. 7 d. 2 e. 2
3. a. 515 b. 18.14 c. 2.2 d. 6580 e. 0.136
4. a. 2 b. 0.4 c. 164 d. 60 e. 7.4
5. a. 30 b. 30 c. 10 d. 0.01 e. 4
6. a. Mass = density \times volume = 8.9 g/cc \times 5.67 cc = 50. g
 b. Density = mass \div volume = 250 g \div 250 cc = 1.0 g/cc
 c. Density = 105.0 g \div 10 cc = 10 g/cc
 d. Volume = mass \div density = 64.30 g \div 2.0 g/cc = 32 cc
7. Experimental error = 7.2 g/cc - 6.8 g/cc = 0.4 g/cc.
 Percentage error = (0.4 g/cc \div 7.2 g/cc) \times (100%) = 6%
8. a. Volume is the independent variable since it is plotted along the horizontal axis.
 b. Mass is the dependent variable since it is plotted along the vertical axis.
 c. The predicted mass of the block at zero volume is zero—no wood, no mass.
 d. Slope = 0.69 g/cc. It is the change in volume divided by the change in mass.
 e. 37 cc.
 f. The density of the wood is 0.69 g/cc; it is the slope of the line. It is the amount in grams that the mass increases for each cc increase in volume. Therefore, density is defined as mass per unit volume.
9. Handbook Answers: (Taken from the 46th edition, 1965-1966.)

Answer	Page No.
a. Ionic radius of gold, +1 = 1.26 Å +2 = 0.89 Å	a. F-117
b. Zinc sulfate, emetics, stomach siphon, white of egg, milk, chalk, castor oil, table salt, reduced iron	b. xxiii
c. By Ulloa in 1735, by Wood in 1741	c. B-126
d. Practically nonflammable Vapor density = 3.55 Boiling point = 48°F Not water soluble; has odor	d. E-20
e. Rhombic	e. B-209
10. It is closed; there are no observable changes.
11. a. The tendency toward randomness is greater than the tendency toward minimum energy.
 b. Same as answer to a.
12. D, since only 4 is correct.

SELF-TEST (pp. 32 to 35)

3. Experimental error = $7.3 \text{ g/cc} - 7.0 \text{ g/cc} = 0.3 \text{ g/cc}$
 Percentage error = $(7.3 \text{ g/cc} \div 0.3 \text{ g/cc}) \times (100\%) = 4\%$

4. a. $\text{Mass} = \text{density} \times \text{volume} = 13.6 \text{ g/cc} \times 9.30 \text{ cc} = 126 \text{ g}$
 b. $\text{Density} = \text{mass} \div \text{volume} = 45.1 \text{ g} \div 5.06 \text{ cc} = 8.91 \text{ g/cc}$
 c. $\text{Volume} = \text{mass} \div \text{density} = 6.70 \text{ g} \div 1.74 \text{ g/cc} = 3.85 \text{ cc}$
5. a. 0.1 m d. 0.1 g
 b. 1.5 liters e. 0.01 m
 c. 500,000 mg f. 0.025 liter
6. a. 2 b. 5 c. 4 d. 5 e. 2 f. 2
7. Your graph should resemble the one shown here. Does it contain all the items of information listed as the rules for graphing given on pages 21 and 22?



- a. Time is the independent variable because the length of time the water cools determines the temperature of the water.
- b. The relationship is linear except during the first six minutes.
- c. 1.9°C/min
- d. The predicted temperature at 26 minutes is 38°C .
- e. Room temperature is usually about 20°C , and the water would not cool below room temperature.
- f. 10°C
- g. 3.5°C/min

8. a. The flow is the independent variable, because it is on the horizontal axis.
- b. 0.63 feet/gallon
- c. The mathematical equation for an increasing linear relationship which passes through the origin is $m = y/x$; in this case $m = 0.63$ feet/gallon, $y = \text{depth}$, and $x = \text{flow}$.
- d. 22 feet
9. (Taken from the *Handbook of Chemistry and Physics*, 46th edition, 1965–1966.)

Answer	Page No.
a. Density = 4.13 g/cc at 18°C	a. B-238
b. Arfvedson	b. B-119
c. Multiply by 0.833333	c. F-162
d. Hexagonal	d. B-169
e. Dissolve SbCl_5 in water	e. D-58
10. *Chemistry, Science World, Journal of Chemical Education, Chemical and Engineering News, and Science News. Scientific American and Saturday Review of Science* are examples of scientifically oriented journals that are published for laymen interested in science and for scientists who want to know what is happening in science, generally.
11. D, since only 4 is correct.

Chapter 2

PRACTICE EXERCISES (pp. 56, 57)

1. Physical: a, b, e, g, i. Chemical: c, d, f, h, j.
2. Physical: b, c, d, f, i, j. Chemical: a, e, g, h.
3. Metallic properties: b, c, d, e.
4. Gaseous properties: a, c, d.
5. Aluminum, 7.5%
6. The Law of Definite Proportions states that every compound has a definite composition by weight. This means that in order to form the compound water, we must always combine hydrogen and oxygen in the weight proportions of 1:8.
7. a. sodium b. mercury c. potassium d. copper e. iron
8. a. Pb b. Ag c. Mg d. Zn e. Sn
9. In the solid state the molecules are in an orderly arrangement in close contact with each other. When paradichlorobenzene melts, randomness is increased but so is energy.
10. The symbol for the element cobalt is Co. The formula for the compound carbon monoxide is CO. This stands for one atom of carbon combined with one atom of oxygen.
11. As like magnetic poles move closer, work must be done to overcome the force of repulsion. This results in an increase in the potential energy of the system.

12. Since there is no plateau, the solid must be a mixture that melts gradually over a range of temperatures. Only pure compounds and elements have sharply defined melting points.
13. B, since the reason does not explain the assertion.

SELF-TEST (pp. 57, 58)

1. Fat can be separated from milk by mechanical processes, such as centrifuging. Water and sugar can be identified in milk without using a chemical method of separating them. So long as the substances can be identified by their characteristic properties and separated by physical processes, the substance is a mixture.
2. Water has completely different physical properties from its components, oxygen and hydrogen, and sugar has different physical properties from its components, hydrogen, carbon, and oxygen. The components of both substances are always present in fixed proportions by weight. However, sugar and water can be mixed in different proportions and retain their own properties when part of a solution.
3. Physical: b, c, e. Chemical: a, d.
4. This is an example of a chemical change; when the colorless solutions are mixed, a new substance appears which has physical properties different from those of the solutions.
5. Oxygen, 49.5%.
6. Sulfur would remain partially unreacted. If a ratio of 7:4 represents a complete reaction between iron and sulfur, then 1.3 g of sulfur would remain after the entire 3 g of iron had combined with 1.7 g of sulfur.
7. The potential energy of the system decreased because attracting objects were moved closer together.
8. a. Mn b. W c. Cl d. Ca e. Ni
9. a. fluorine b. gold c. helium d. nitrogen e. carbon
10. C, since the magnets will move apart but *potential* energy will change to *kinetic* energy.

Chapter 3

PRACTICE EXERCISES (pp. 89 to 91)

1. Refer to figure on p. 41.
2. Molecules in liquids are close enough together so that any given molecule making its way through the liquid will keep colliding with other molecules. As a result molecules travel a much longer distance than the straight line path between two points as they diffuse.
3. The one heated to 50°C, because raising the temperature of the liquid raises its vapor pressure. The higher the vapor pressure, the more rapid the rate of evaporation.
4. The system must be closed; no observable changes can be seen; two opposing processes are going on at the same rate.

5. The molecules that leave the liquid during evaporation are the ones with the highest energies. When they leave, the average kinetic energy of the molecules in the liquid is lowered, and the temperature of the liquid is thus reduced.
6. Equilibrium: b, c. Steady State: a, d.
7. The lower the boiling point, the higher the vapor pressure at room temperature; so in order of decreasing vapor pressure: ethyl chloride, methanol, carbon tetrachloride, phenol.
8. a. favors liquid; b. favors gas; c. favors gas; d. favors liquid.
9. The vapor pressure at which a liquid and its vapor are exchanging molecules at equal rates.
10. Solute is uniformly distributed, solute and solvent are mixed at the molecular level, solution cannot be separated by filtration, solution will not separate on standing.
11. When a solid dissolves in a liquid, the particles become less orderly and more random. But molecules are much more random in the gaseous phase than when they become confined in a liquid solution.
12. There is a 104.45° angle between the bonds joining the hydrogens to the oxygen. The oxygen end of the molecule tends to be negative; the hydrogen ends of the molecule are slightly positive. The molecule is called polar because its ends have opposite charges.
13. See Sec. 3-5.
14. See Secs. 3-1, 3-4, 3-6, and 3-7.
15. Hydrogen gas and calcium hydroxide, a base.
16. Rusting of iron, sprouting of seeds, cleansing of hands and clothing, etc.
17. Much more heat is required to change the temperature of a body of water than is required to change the temperature of a land mass of similar size. Therefore, temperatures change much more slowly near large bodies of water.
18. Above 4°C , the molecules have enough kinetic energy to move further and further apart; below 4°C , the molecules tend to form clusters that contain open spaces. In both cases water becomes less dense than at 4°C .
19. a. 164.1 g b. 28.1 g c. 17.8 g d. 36.0 g

SELF-TEST (pp. 91, 92)

1. (d) 4°C
2. (b) gain of potential energy. There is no change in kinetic energy if the liquid is at the same temperature as its surroundings.
3. 4.3 g
4. a. $\text{Ce}_2(\text{SO}_4)_3$ b. 22 g c. 40 g of NaCl for each 100 g of water
5. Diethyl ether, carbon disulfide, benzene, ethanol, acetic acid.
6. (a) saturated
7. a. gas b. liquid c. gas
8. It requires 540 calories of heat to change one gram of water at 100°C into steam at the same temperature. This heat must be converted to potential energy, as the kinetic energy does not change when the temperature remains the same.

9. Climate B, because the upper layer of water is so much less dense than the cold layer beneath that there is virtually no mixing until the fall turn-over.
10. See Sec. 3-5.
11. A, since the assertion is correct and the reason correctly explains it.

Chapter 4

PRACTICE EXERCISES (p. 118)

1. a. neutral b. acidic c. neutral d. basic e. neutral
2. a. 1 b. 4 c. 0
3. Acetic acid-sodium acetate solution. At equilibrium the solution contains a relatively large number of acetic acid molecules and acetate ions compared to the number of hydronium ions. If hydroxide ions are added, they react with hydronium ions. Acetic acid molecules then break up to supply more hydronium ions, thus returning the solution to equilibrium. If extra hydronium ions are added, the acetate ions react with them to form acetic acid molecules, thus returning the solution to equilibrium.
4. Acid: a proton donor. Base: a proton acceptor. Examples: acid, HCl; base, OH⁻.
5. Ammonia, because it more readily accepts a proton from water:
$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-.$$
6. They react with fatty tissue under the skin to produce soap.
7. Check the color of litmus in their presence, or use hydron paper.
8. a. sodium hydroxide e. carbonic acid
b. nitric acid f. copper sulfate
c. acetic acid g. potassium bromide
d. potassium hydroxide
9. Adding acetate ions will shift the equilibrium to the left as they react with H₃O⁺ ions. This reduces the acidity of the solution until a new equilibrium has been established.
10. It gives a much more precise value for pH. Litmus merely indicates whether the solution is acidic or basic.
11. A strong electrolyte is completely ionized in solution and conducts electricity well. A weak electrolyte is only partially ionized in solution and conducts electricity poorly.
12. C, since 2 and 4 are correct.

SELF-TEST (pp. 118, 119)

1. See Secs. 4-1, 4-2, 4-11, 4-13.
2. a. hydrochloric acid c. hydrosulfuric acid
b. sulfuric acid d. hydrobromic acid
3. a. calcium hydroxide c. magnesium hydroxide
b. barium hydroxide
4. a. sodium nitrate b. magnesium chloride c. calcium sulfate

5. a. neutral b. neutral c. neutral d. basic
6. a. 0.00000001 b. 0.01 c. 0.0000001 d. 0.1
7. Most acids, bases, and salts form ions in solution, so the solution can conduct a current. Carbon tetrachloride does not form any ions in solution, and when no ions are present, the solution cannot conduct a current.
8. See Secs. 4-5 and 4-8.
9. Mix an acid solution with a basic solution.
10. HCl ionizes completely in water solution. Ammonia water does not form as many ions in solution and therefore cannot conduct a current as well as HCl.
11. D, since water is a weaker base than ammonia, but the reason is a true statement.

Chapter 5

PRACTICE EXERCISES (p. 151)

1. A "black box" is a problem that we must solve by gathering indirect evidence.
2. See Sec. 5-3.
3. Dalton viewed the atom as an indestructible unit. The discovery of smaller particles within the atom meant that it is not the ultimate unit of matter.
4. See Sec. 5-8.
5. (a) Richard and Soddy discovered isotopes. (b) Planck proposed that light is emitted in small packages, or "quanta." (c) Avogadro proposed that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. (d) Millikan devised the necessary experimental apparatus and then used it to determine the charge on the electron. (e) Democritus was the first to propose that matter is composed of atoms.
6. (a) red (b) bright green (c) persistent yellow
7. (a) brown (b) blue (c) violet
8. Radiant energy waves may be transmitted through a vacuum, whereas sound waves must be transmitted through a medium (air, water, wood, etc.).
9. For the same weight of nitrogen, NO_2 contains exactly twice as much oxygen by weight as does NO .
10. Answers vary.
11. A, since the reason correctly explains the assertion.

SELF-TEST (pp. 151, 152)

1. Answers vary: cancer; common cold; origin of life; etc.
2. See Sec. 5-3.
3. Rutherford's discovery that alpha particles could bounce straight back from a piece of thin gold foil.
4. (a) Dalton proposed that the atom is the ultimate particle of matter, proposed the Law of Multiple Proportions, and determined the first crude

values of atomic weight. (b) Thomson discovered the electron. (c) Becquerel discovered that certain ores emit radioactive rays. (d) Bohr proposed that there are "permitted" energy levels for electrons in atoms. (e) Rutherford discovered the nucleus of the atom.

5. See Sec. 5-14.
6. (a) orange (b) violet (c) greenish-yellow
7. (a) green (b) blue (c) brown
8. See Sec. 5-9.
9. For the same weight of carbon, CO_2 contains exactly twice as much oxygen by weight as does CO.
10. See Sec. 5-7.
11. A, since only 1, 2, and 3 are correct.

Chapter 6

PRACTICE EXERCISES (pp. 172, 173)

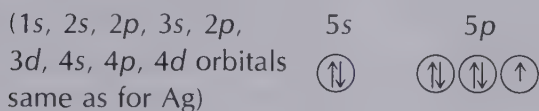
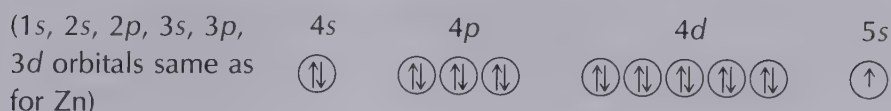
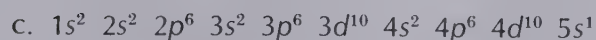
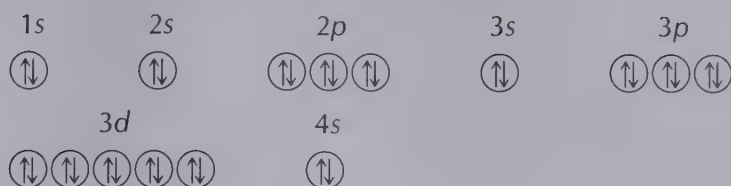
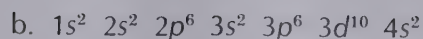
1. a. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
 b. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$
 c. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$
 d. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2$
2.

	1s	2s	2p	3s	3p
a. ${}_3\text{Li}$	$\uparrow\downarrow$	\uparrow	○ ○ ○		
b. ${}_6\text{C}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ ○ ○		
c. ${}_{12}\text{Mg}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	○ ○ ○
d. ${}_{17}\text{Cl}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow
3. a. $\dot{\text{H}}$ b. $\dot{\text{Na}}$ c. $\ddot{\text{Al}}\cdot$ d. $\cdot\ddot{\text{S}}:$
4. a. F b. A c. C and D d. F e. E and F
5. A, since the reason correctly explains the assertion.

SELF-TEST (pp. 173, 174)

1. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$





2. a. The atomic radius increases, because there are more energy levels.
b. The ionization energy decreases, because the outer electron is farther from the positive nucleus.
3. a. Same as answer to 2 a.
b. Same as answer to 2 b.
4. a. The atomic radius decreases, because the nuclear attraction increases as the atomic number increases.
b. The ionization energy increases, again because the nuclear attraction increases as the atomic number increases.
5. (1) It does not show the arrangement of the electrons within the atom.
(2) The sphere has rigid boundaries and atoms do not.
6. Moseley's work showed that each element had a unique atomic number, equal to the number of protons in its nucleus. When the elements are arranged in order of increasing atomic number, a pattern of regularly recurring properties appears.
7. The effect for all families is the same as in Questions 2 and 3. The effect for all periods is the same as in Question 4.
8. Advantages: (1) Simplifies our study of the elements by grouping those with similar properties. (2) Enables us to apply trends in making predictions about the properties of elements and their compounds. (3) Enables

us to compare the properties of metals and nonmetals.

Disadvantages: (1) There is no proper place for hydrogen. (2) The lanthanide and actinide series must be placed apart from the rest of the elements.

9. a. A b. A c. E d. D and E e. E
10. E, since only 1 and 4 are correct.

Chapter 7

PRACTICE EXERCISES (p. 197)

- Any force which tends to hold atoms together.
 - A property which indicates the amount of attraction an atom holds for electrons; it is useful in predicting the type of bond occurring between two atoms.
 - Energy required to remove the most loosely bound electron from a neutral atom; the value of this energy indicates the ease with which an atom becomes a positive ion.
 - A bond that is between a highly electronegative atom on one molecule and a hydrogen atom that is already bonded to a highly electronegative atom on another molecule.
- In the halogen family, increasing atomic number results in decreasing ionization energy because with each increase in atomic number within a family there is an additional energy level. As levels are added and electrons become farther from the nuclear pull of protons, it requires less energy to pull the electron away.
 - In period 3, the ionization energies increase with atomic number because the same energy level is filling with electrons while more nuclear pull is being exerted with the addition of more protons. There are, however, irregularities in the increase of ionization energies because of the pairing of electrons in orbitals.
- Group 1A shows an increase in atomic radius with the increase of atomic number due to the addition of another energy level with each increase in atomic number.
 - In period 4 the atomic radius decreases irregularly with the increase of atomic number. This is because in any period as atomic number increases, the same energy level is filling while the nucleus is also gaining more protons. The additional nuclear pull causes the electrons to draw closer to the nucleus, decreasing the atomic size.
- Polar covalent, because the difference in electronegativities is 0.5.
 - Nonpolar covalent, because like atoms form nonpolar covalent bonds.
 - Ionic, because the difference in electronegativities is 2.2.
 - Polar covalent, because the difference in electronegativities is 0.4.
- Ionic, because the difference in electronegativities is 2.0.
 - Ionic, because the difference in electronegativities is 2.5.
 - Polar covalent, because the difference in electronegativities is 0.5.

- SELF-TEST** (pp. 197, 198)

1. The ionic radius of F^- is smaller than that of Cl^- , so the Na^+ ion can get closer to the center of the F^- ions and the attraction is greater. Therefore it requires more energy (a higher temperature) to melt NaF .
2. On the basis of electronegativities, the following bond types are predicted.
Ionic: Rb_2O , $CaCl_2$, BaO Covalent: NaI , SO_2
3.
 - a. Any force which tends to hold atoms together.
 - b. A rather weak bond between molecules due to the attraction between positive and negative charges on neighboring molecules.
 - c. A strong chemical bond formed by transfer of electrons.
 - d. The formula for an ionic compound; tells the simplest ratio in which ions exist in the compound.
 - e. An atom (or group of atoms) with a net electric charge due to loss or gain of electrons.
4.

a.	b.	c.	d.
$\ddot{O}:\ddot{C}:\ddot{O}:$	$\begin{array}{c} \ddot{S}:\ddot{H} \\ \\ H \end{array}$	$Ag:\ddot{Cl}:$	$H:H$
5. (1) The resulting combination has less energy than the separate atoms.
(2) The atoms achieve the electron configurations of the nearest noble gases.
6. Van der Waals, because the attractive forces between molecules are weak and not much energy is needed to melt the compound.
7. For nonmetals the electronegativity values are high. They increase from left to right in the periodic table and decrease from top to bottom.
8. An oxygen molecule has less energy than two separated oxygen atoms. When two atoms form a bond, energy is released and the resulting combination has less energy.

9. a. Cl_2 ; nonpolar covalent (based on electronegativity difference)
 b. KI ; polar covalent "
 c. CaCl_2 ; ionic "
 d. CuS ; polar covalent "
 e. AlCl_3 ; polar covalent "
 10. C, because only 2 and 4 are correct.

Chapter 8

PRACTICE EXERCISES (pp. 221, 222)

1. a. FeSO_4 b. $\text{Pb}(\text{NO}_3)_2$ c. CS_2 d. MnO_2 e. SO_3
 2. a. copper(II) nitrate d. manganese(V) oxide or dimanganese pentoxide
 b. mercury(II) chloride e. nitrogen(I) oxide or dinitrogen monoxide
 c. calcium oxide
 3. a. K: $39.1 \times 1 = 39.1$
 Cl: $35.5 \times 1 = 35.5$
 O: $16.0 \times 3 = \underline{48.0}$
 122.6
 d. Ag: $107.9 \times 1 = 107.9$
 Cl: $35.5 \times 1 = \underline{35.5}$
 143.4
 b. Al: $27.0 \times 1 = 27.0$
 N: $14.0 \times 3 = 42.0$
 O: $16.0 \times 9 = \underline{144.0}$
 213.0
 e. K: $39.1 \times 1 = 39.1$
 Mn: $54.9 \times 1 = 54.9$
 O: $16.0 \times 4 = \underline{64.0}$
 158.0
 c. Na: $23.0 \times 2 = 46.0$
 S: $32.1 \times 1 = 32.1$
 O: $16.0 \times 4 = \underline{64.0}$
 142.1
 4. a. 4 moles
 b. formula weight of HNO_3
 H: $1.0 \times 1 = 1.0$
 N: $14.0 \times 1 = 14.0$
 O: $16.0 \times 3 = \underline{48.0}$
 63.0
 Since 1 mole of HNO_3 weighs 63.0 g, then 4 moles weigh $63.0 \text{ g} \times 4 = 252 \text{ g}$.
 c. 2 moles
 d. 2 atoms
 5. a. 1 mole
 b. 40.1 g
 c. $\frac{4}{40.1} \text{ Ca} + ??\text{H}_2\text{O} \rightarrow ??\text{Ca}(\text{OH})_2 + ??\text{H}_2$
 number of moles of $\text{Ca}(\text{OH})_2 = \frac{4}{40.1} = 0.1$

d. formula weight of Ca(OH)_2

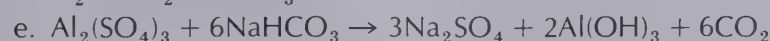
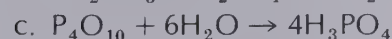
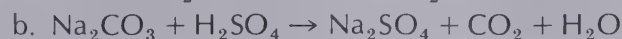
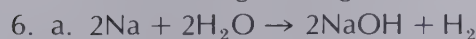
$$\text{Ca: } 40.1 \times 1 = 40.1$$

$$\text{O: } 16.0 \times 2 = 32.0$$

$$\text{H: } 1.0 \times 2 = \frac{2.0}{74.1}$$

Since 1 mole of Ca(OH)_2 weighs 74.1 g, then 0.1 mole weighs

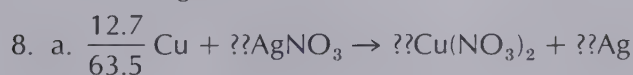
$$0.1 \times 74.1 \text{ g} = 7.4 \text{ g.}$$



7. a. synthesis d. decomposition

b. decomposition e. ion-ion

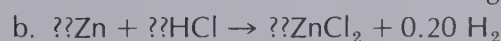
c. rearrangement



$$\text{number of moles of silver} = 2 \times \frac{12.7}{63.5} = 0.40$$

b. number of grams of silver = $0.40 \times 107.9 \text{ g} = 43.1 \text{ g}$

9. a. number of moles of $\text{H}_2 = \frac{0.40 \text{ g}}{2 \times 1.0 \text{ g}} = 0.20$



$$\text{number of moles of zinc} = 0.20$$

c. number of grams of zinc = $0.20 \times 65.4 \text{ g} = 13.1 \text{ g}$

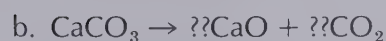
10. a. formula weight of CaCO_3

$$\text{Ca: } 40.1 \times 1 = 40.1$$

$$\text{C: } 12.0 \times 1 = 12.0$$

$$\text{O: } 16.0 \times 3 = \frac{48.0}{100.1}$$

$$\text{number of moles of } \text{CaCO}_3 = \frac{159.0 \text{ g}}{100.1 \text{ g}} = 1.59$$



$$\text{number of moles of } \text{CO}_2 = 1.59$$

c. formula weight of CO_2

$$\text{C: } 12.0 \times 1 = 12.0$$

$$\text{O: } 16.0 \times 2 = \frac{32.0}{44.0}$$

$$\text{number of grams of } \text{CO}_2 = 1.59 \times 44.0 \text{ g} = 70.0 \text{ g}$$

11. E, since all 4 choices are correct.

SELF-TEST (pp. 222, 223)

1. a. 149.0 g b. 120.4 g c. 138.2 g d. 232.8 g e. 108.0 g

2. a. I_2 b. ZnCl_2 c. CuS d. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ e. $\text{Ba}_3(\text{PO}_4)_2$

3. a. iron(II) chloride

b. aluminum sulfate

- c. nitrogen(III) oxide or dinitrogen trioxide
 d. manganese(IV) oxide or manganese dioxide
 e. chromium(III) oxide or dichromium trioxide
4. a. $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$; synthesis
 b. $2\text{K} + 2\text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{H}_2$; rearrangement
 c. $2\text{PbO}_2 \rightarrow 2\text{PbO} + \text{O}_2$; decomposition
 d. $\text{Cu} + 2\text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$; metal-ion
 e. $2\text{Al}(\text{NO}_3)_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{HNO}_3$; rearrangement
5. a. 196 g Zn is 3 moles, so 3 moles H_2 will form.
 b. 3 moles H_2 weighs 6.0 g.
6. 106.8 g
7. a. formula weight SO_2
 S: $32.1 \times 1 = 32.1$
 O: $16.0 \times 2 = \underline{32.0}$
 64.1
 weight of 3 moles $\text{SO}_2 = 3 \times 64.1 \text{ g} = 192 \text{ g}$
- b. $??\text{S} + ??\text{O}_2 \rightarrow 3\text{SO}_2$
 3 moles of O_2 are required.
- c. 3 moles of S are required.
- d. weight of 3 moles S = $3 \times 32.1 \text{ g} = 96.1 \text{ g}$
8. a. number of moles of $\text{H}_2 = \frac{6.0 \text{ g}}{2 \times 1.0 \text{ g}} = 3.0$
 b. $??\text{Ca} + ??\text{H}_2\text{O} \rightarrow ??\text{Ca}(\text{OH})_2 + 3.0 \text{ H}_2$
 number of moles of Ca = 3.0
 c. number of grams of Ca = $3.0 \times 40.1 \text{ g} = 120 \text{ g}$
9. a. weight of 1.5 moles $\text{O}_2 = 1.5 \times 2 \times 16.0 \text{ g} = 48.0 \text{ g}$
 b. $??\text{KClO}_3 \rightarrow ??\text{KCl} + 1.5\text{O}_2$
 number of moles $\text{KClO}_3 = 1.0$
 c. formula weight KClO_3
 K: $39.1 \times 1 = 39.1$
 Cl: $35.5 \times 1 = 35.5$
 O: $16.0 \times 3 = \underline{48.0}$
 122.6
 number of grams of $\text{KClO}_3 = 1.0 \times 122.6 \text{ g} = 122.6 \text{ g}$
10. A, since the reason correctly explains the assertion.

Chapter 9

PRACTICE EXERCISES (pp. 243, 244)

1. $V_1 = 250 \text{ cc}$ $P_1 = 700 \text{ torr}$
 $V_2 = 200 \text{ cc}$ $P_2 = ?$

Note that a reduction in volume is caused by increased pressure.

$$V_1 P_1 = V_2 P_2; P_2 = P_1 \times \frac{V_1}{V_2} = 700 \text{ torr} \times \frac{250 \text{ cc}}{200 \text{ cc}} = 875 \text{ torr}$$

2. $V_1 = 50 \text{ cc}$ $T_1 = 0^\circ\text{C} = (0 + 273)^\circ\text{K} = 273^\circ\text{K}$
 $V_2 = 100 \text{ cc}$ $T_2 = ?$
 $\frac{V_1}{T_1} = \frac{V_2}{T_2}$; since the volume is doubled, the temperature is also doubled,
to $546^\circ\text{K} = (546 - 273)^\circ\text{C} = 273^\circ\text{C}$.
3. $V_1 = 300 \text{ cc}$ $T_1 = 20^\circ\text{C} = (20 + 273)^\circ\text{K} = 293^\circ\text{K}$
 $V_2 = ?$ $T_2 = 25^\circ\text{C} = (25 + 273)^\circ\text{K} = 298^\circ\text{K}$
 $P_1 = 750 \text{ torr}$
 $P_2 = 770 \text{ torr}$
 $V_2 = 300 \text{ cc} \times \frac{750 \text{ torr}}{770 \text{ torr}} \times \frac{298^\circ\text{K}}{293^\circ\text{K}} = 297 \text{ cc}$
4. $V_1 = 100 \text{ cc}$ $T_1 = 25^\circ\text{C} = (25 + 273)^\circ\text{K} = 298^\circ\text{K}$
 $V_2 = ?$ $T_2 = 0^\circ\text{C} = (0 + 273)^\circ\text{K} = 273^\circ\text{K}$
 $P_1 = 740 \text{ torr}$
 $P_2 = 760 \text{ torr}$
 $V_2 = 100 \text{ cc} \times \frac{740 \text{ torr}}{760 \text{ torr}} \times \frac{273^\circ\text{K}}{298^\circ\text{K}} = 89 \text{ cc}$
5. Pressure of dry hydrogen at $25^\circ\text{C} = 675 \text{ torr} - 24 \text{ torr} = 651 \text{ torr}$
 $V_1 = 25 \text{ cc}$ $T_1 = 25^\circ\text{C} = 298^\circ\text{K}$
 $V_2 = ?$ $T_2 = 0^\circ\text{C} = 273^\circ\text{K}$
 $P_1 = 651 \text{ torr}$
 $P_2 = 760 \text{ torr}$
 $V_2 = 25 \text{ cc} \times \frac{651 \text{ torr}}{760 \text{ torr}} \times \frac{273^\circ\text{K}}{298^\circ\text{K}} = 19 \text{ cc}$
6. 1 liter at S.T.P. is $(1/22.4)$ mole, since one mole occupies 22.4 liters.
1 mole weighs 64.0 g, so 1 liter at S.T.P. weighs $\frac{1}{22.4} \times 64.0 \text{ g} = 2.86 \text{ g}$.
7. 1 mole weighs 34.0 g and occupies 22.4 liters at S.T.P., so the density is
 $\frac{34.0 \text{ g}}{22.4 \text{ liters}} = 1.52 \text{ g/liter}$
8. The weight of 22.4 liters, or 22,400 cc, is
 $0.179 \text{ g} \times \frac{22,400 \text{ cc}}{250 \text{ cc}} = 16.0 \text{ g}$.
Therefore, the molecular weight is 16.0.
9. a. 2.5 moles
b. One mole of molecules of *any* substance contains 6.02×10^{23} molecules.
10. a. Since 122.5 g is the weight of one mole of KClO_3 , then $\frac{3}{2}$, or 1.5, moles of O_2 would be produced.
b. $1.5 \times 32.0 \text{ g} = 48.0 \text{ g}$.
11. A, since the reason correctly explains the assertion.

SELF-TEST (pp. 244, 245)

- See Sec. 9-2.
- Gases can be compressed into smaller volumes because there is so much empty space between molecules.

3. Standard temperature and pressure—0°C and 760 torr.
4. At extremely high pressures the molecules are fairly close together, almost as in a liquid, and the volume of the molecules themselves affects the relationship between volume and pressure.
5. The pressure of the dry gas at 23°C is 675 torr – 21 torr = 654 torr.

$$V_1 = 200 \text{ cc} \quad T_1 = 23^\circ\text{C} = (23 + 273)^\circ\text{K} = 296^\circ\text{K}$$

$$V_2 = ? \quad T_2 = 0^\circ\text{C} = 273^\circ\text{K}$$

$$P_1 = 654 \text{ torr}$$

$$P_2 = 760 \text{ torr}$$

$$V_2 = 200 \text{ cc} \times \frac{654 \text{ torr}}{760 \text{ torr}} \times \frac{273^\circ\text{K}}{296^\circ\text{K}} = 158 \text{ cc}$$

6. a. 150 liters, since a volume of H₂O equal to that of H₂ is produced.
- b. $\frac{150}{22.4} = 6.7$
- c. The same number, 6.7.
- d. Since the molecular weight of water is 18.0, the weight of 6.7 moles is $6.7 \times 18.0 \text{ g} = 120 \text{ g}$.

$$7. \text{ Density} = \frac{0.35 \text{ g}}{130 \text{ cc}} = 0.0027 \text{ g/cc}$$

$$\text{The weight per mole is } 0.35 \text{ g} \times \frac{22,400 \text{ cc}}{130 \text{ cc}} = 60 \text{ g}.$$

8. The temperature and pressure increase in proportion to each other. There are any number of correct answers, including 1520 torr and 546°K (pressure and temperature doubled), and 380 torr and 137°K (pressure and temperature halved). If the container volume were flexible, it would mean that more pressure would have to be applied as the sample was heated, or the pressure reduced if the sample was cooled.
9. The increase in temperature as the sun warmed the beverage decreased the solubility of the carbon dioxide and increased the amount of it that was in the form of a gas at equilibrium. In addition, the temperature increased the pressure of the gas and the vapor pressure of the water increased. The bottle burst when it could no longer withstand the increased pressure.
10. Weight of 22.4 liters is $22.4 \text{ liters} \times 1.53 \text{ g/liter} = 34.3 \text{ g}$. Therefore, molecular weight = 34.3.
11. Molecular weight H₂S

$$\text{H: } 1.0 \times 2 = 2.0$$

$$\text{S: } 32.0 \times 1 = \underline{32.0}$$

$$34.0$$

$$\text{Density} = \frac{34.0 \text{ g}}{22.4 \text{ liters}} = 1.52 \text{ g/liter}.$$

12. E, since 1, 2, and 4 are correct.

Chapter 10

PRACTICE EXERCISES (pp. 269, 270)

- See Sections 10-1 to 10-7.
- As ice melts, the orderly arrangement of the molecules is destroyed, resulting in a random arrangement that is characteristic of liquids. However, the potential energy of the molecules increases (while the kinetic energy remains the same). So, melting achieves a more random state at the expense of minimum energy.
- molecular
 - molecular
 - ionic
 - metallic
 - ionic
- See Sec. 10-6.
- Deliquescence is the ability of a solid to pick up water from the atmosphere. Calcium chloride is one such solid. Deliquescent solids can be used to keep things dry in humid environments.
- At 4°C the molecules are as close together as they can get. Above this temperature, increased kinetic energy moves them farther apart and the density is less. Below 4°C, more and more hydrogen bonds form. This causes the molecules to assume an arrangement in which there is a great deal of open space, thus decreasing density.
- $\text{Ba}_{(\text{aq})}^{2+} + 2\text{Cl}_{(\text{aq})}^{-} + 2\text{Ag}_{(\text{aq})}^{+} + 2\text{NO}_{3(\text{aq})}^{-} \rightarrow \text{Ba}_{(\text{aq})}^{2+} + 2\text{NO}_{3(\text{aq})}^{-} + 2\text{AgCl}_{(\text{s})}$
 - $2\text{Na}_{(\text{aq})}^{+} + \text{CO}_{3(\text{aq})}^{2-} + \text{Pb}_{(\text{aq})}^{2+} + 2\text{NO}_{3(\text{aq})}^{-} \rightarrow 2\text{Na}_{(\text{aq})}^{+} + 2\text{NO}_{3(\text{aq})}^{-} + \text{PbCO}_{3(\text{s})}$
 - $2\text{NH}_{4(\text{aq})}^{+} + \text{S}_{(\text{aq})}^{2-} + \text{Ni}_{(\text{aq})}^{2+} + 2\text{Cl}_{(\text{aq})}^{-} \rightarrow 2\text{NH}_{4(\text{aq})}^{+} + 2\text{Cl}_{(\text{aq})}^{-} + \text{NiS}_{(\text{s})}$
- A, since 1, 2, and 3 are correct.
- E, since 1, 2, and 4 are correct.

SELF-TEST (p. 270)

- They are held together by the weak van der Waals forces, and little energy is required to separate them.
- H_2O
 - Na
 - Ar
 - H_2O
- (a) Solids have definite shape because the particles vibrate around fixed positions and are not free to move about. (b) Solids do not diffuse to any appreciable extent because of the fact that the particles remain near fixed positions. (c) Crystals form because the particles form bonds with all their neighbors and this results in an orderly arrangement.
- metallic
 - ionic
 - molecular
 - network solid
 - molecular
 - ionic
- Calcium chloride is deliquescent when the water vapor pressure in the crystal is less than that in the atmosphere. The crystal absorbs water until the vapor pressures are equal.
- See Sec. 10-6.
- As a solid melts, the particles absorb energy and become more random. Thus, randomness is achieved at the expense of minimum energy.

8. See Exp. 10-1.
9. a. $\text{Ba}_{(\text{aq})}^{2+} + 2\text{Cl}_{(\text{aq})}^{-} + 2\text{Na}_{(\text{aq})}^{+} + \text{SO}_{4(\text{aq})}^{2-} \rightarrow 2\text{Na}_{(\text{aq})}^{+} + 2\text{Cl}_{(\text{aq})}^{-} + \text{BaSO}_{4(\text{s})}$
 b. $2\text{NH}_{4(\text{aq})}^{+} + \text{S}_{(\text{aq})}^{2-} + \text{Co}_{(\text{aq})}^{2+} + 2\text{Cl}_{(\text{aq})}^{-} \rightarrow 2\text{NH}_{4(\text{aq})}^{+} + 2\text{Cl}_{(\text{aq})}^{-} + \text{CoS}_{(\text{s})}$
 c. $2\text{Ag}_{(\text{aq})}^{+} + 2\text{NO}_{3(\text{aq})}^{-} + 2\text{K}_{(\text{aq})}^{+} + \text{CrO}_{4(\text{aq})}^{2-} \rightarrow 2\text{K}_{(\text{aq})}^{+} + 2\text{NO}_{3(\text{aq})}^{-} + \text{Ag}_2\text{CrO}_{4(\text{s})}$
10. A, because the reason correctly explains the assertion.

Chapter 11

PRACTICE EXERCISES (pp. 281, 282)

- $\text{Cl}_2 + 2\text{NaI} \rightarrow 2\text{NaCl} + \text{I}_2$
 - $\text{H}_2\text{S} + \text{HgCl}_2 \rightarrow 2\text{HCl} + \text{HgS}$
 - $6\text{NH}_4\text{OH} + \text{Al}_2(\text{SO}_4)_3 \rightarrow 3(\text{NH}_4)_2\text{SO}_4 + 2\text{Al}(\text{OH})_3$
 - $(\text{NH}_4)_2\text{S} + \text{Ni}(\text{NO}_3)_2 \rightarrow 2\text{NH}_4\text{NO}_3 + \text{NiS}$
- Pb^{2+}
 - Fe^{3+}
- I^{-}
 - CO_3^{2-}
- (a) greenish-yellow; (b) violet; (c) red; (d) yellow (persistent)
- (a) green; (b) pink; (c) blue
- (a) brown; (b) blue; (c) green
- Cl_2 : frees the Br^{-} or I^{-} by giving up an electron to it. This forms Br_2 or I_2 molecules.
 CCl_4 : dissolves I_2 or Br_2 to give a characteristic color.
- NH_4Cl supplies a common ion, NH_4^{+} , and keeps the solution slightly basic.
- Na_2CO_3 precipitates the cation and places the anion in solution. All sodium compounds are soluble in water.
- Because they precipitate with the reagents used to test for anions and would, therefore, interfere with the tests for the anions.
- When an equilibrium system is subjected to a stress, the system reacts in such a way as to relieve the stress. For example, when two solutions are mixed and an insoluble compound forms, the compound will precipitate out. (Examples vary.)
- Unless the solution containing Group II cations is slightly acidic, the cations will not precipitate upon the addition of H_2S .
- E; the solutions must be *acidic* because the compounds are soluble in *basic* solutions.

SELF-TEST (pp. 282, 283)

- $\text{Na}_2\text{CO}_3 + \text{CoCl}_2 \rightarrow \text{CoCO}_3 + 2\text{NaCl}$
 - $\text{H}_2\text{S} + \text{CuSO}_4 \rightarrow \text{CuS} + \text{H}_2\text{SO}_4$
 - $(\text{NH}_4)_2\text{S} + \text{Mn}(\text{NO}_3)_2 \rightarrow \text{MnS} + 2\text{NH}_4\text{NO}_3$
 - $\text{K}_2\text{CrO}_4 + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{CrO}_4 + \text{K}_2\text{SO}_4$
- cobalt
 - aluminum
- sulfate
 - nitrate
- (a) red; (b) yellow; (c) green; (d) violet
- (a) green; (b) blue

6. (a) green; (b) deep blue; (c) brown
7. The Cl_2 molecules react with the iodide ions to form iodine molecules, which dissolve in CCl_4 to give a characteristic violet solution.
8. HCl makes the solution acidic, so that the sulfides of the Group II cations can precipitate.
9. The ammonium ions from the NH_4Cl buffer the solution and help it to remain basic, so that the sulfides of the Group IV cations can precipitate.
10. AgNO_3 reacts with Group III anions to form a precipitate containing silver.
11. Le Chatelier's Principle states that if a system in equilibrium is disturbed, changes occur which tend to bring the system to a new equilibrium. It is the basis for the common-ion solutions used to maintain a certain pH in testing for certain ions. (Examples vary.)
12. E, since 1, 2, and 4 are correct.

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